

UNCLASSIFIED

AD NUMBER
ADB031741
NEW LIMITATION CHANGE
TO Approved for public release, distribution unlimited
FROM Distribution authorized to U.S. Gov't. agencies only; Test and Evaluation; JUL 1973. Other requests shall be referred to Air Force Rocket Propulsion Laboratory, Attn: STINFO/XOJ, Edwards AFB, CA 93523.
AUTHORITY
afrpl ltr 13 may 1986

THIS PAGE IS UNCLASSIFIED

✓

**LEVEL**

②

AFRPL-TR-78-55 ✓

**MODIFIED HDA CHARACTERIZATION STUDY**

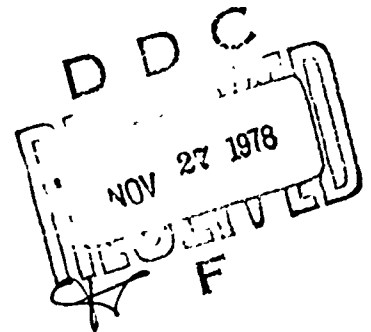
Final Technical Report for Period May 1977-April 1978

BELL AEROSPACE TEXTRON  
P.O. Box 1  
Buffalo, New York 14240

Henry Ph. Heubusch

August 1978

Distribution limited to U.S. Government agencies only;  
Test and Evaluation, July 1973.  
Other Requests for this document must be referred to  
AFRPL (STINFO)/XOJ, Edwards AFB CA 93523.



ADB031741

DDC FILE COPY

Prepared for  
AIR FORCE ROCKET PROPULSION LABORATORY  
DIRECTOR OF SCIENCE AND TECHNOLOGY  
AIR FORCE SYSTEMS COMMAND  
EDWARDS AFB, CALIFORNIA 93523

11 17 00

## NOTICES

When U.S. Government drawings, specifications, or other data are used for any purpose other than a definitely related government procurement operation, the Government thereby incurs no responsibility nor any obligation whatsoever, and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications or other data, is not to be regarded by implementation or otherwise, as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use or sell any patented invention that may in any way be related thereto.

## FOREWORD

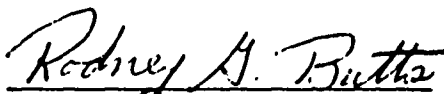
This report covers work sponsored by the Air Force Rocket Propulsion Laboratory, Edwards Air Force Base, California under Contract F04611-77-C-0033 on: 305810VZ. The period of performance was May 1977 to April 1978. During this period Lt. R.G. Butts (LKCP) provided technical direction and administrative functions for AFRPL.

The work was carried out by Bell Aerospace Textron in the Chemistry Department of the Engineering Laboratories. Mr. Henry Ph. Heubusch performed the duties of Program Manager and Technical Director.

Other principal contributors to the success of the program were Dr. L.D. Nasiak and Messrs.: A.M. Gritzmacher, S.A. Long, J.C. Tynan and P.Y. Yin.

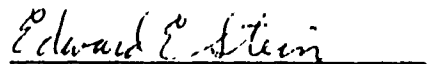
This report was submitted by Mr. Heubusch. The contractor's secondary report number is 8811-927001.

This technical report is approved for release and distribution in accordance with the distribution statement on the cover and on the DD Form 1473.

  
RODNEY G. BUTTS, 1st Lt., USAF  
Project Manager

  
FORREST S. FORBES, Chief  
Propellant Systems Section

FOR THE COMMANDER

  
EDWARD E. STEIN, Deputy Chief,  
Liquid Rocket Division

19 REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER AFRPLTR-78-55	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) MODIFIED HDA CHARACTERIZATION STUDY		5. TYPE OF REPORT & PERIOD COVERED Special Technical Report Period May '77 to April '78
7. AUTHOR(s) Henry Pl. Heubusch		6. PERFORMING ORG. REPORT NUMBER 8811-927001
9. PERFORM. ORGANIZATION NAME AND ADDRESS Bell Aerospace Textron P.O. Box 1 Buffalo, New York 14240		8. CONTRACT OR GRANT NUMBER(s) F04611-77-C-0033
11. CONTROLLING OFFICE NAME AND ADDRESS Air Force Rocket Propulsion Laboratory/LKCP Edwards Air Force Base, California 93523		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS Project 3058 Task 10
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) Final Report May 11, 1978		12. REPORT DATE 30 August 1978
		13. NUMBER OF PAGES 152
		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE N/A
16. DISTRIBUTION STATEMENT (of this Report) Distribution limited to U.S. Government agencies only; Test and Evaluation, July 1973. Other requests for this document must be referred to AFRPL (STINFO)/XOJ, Edwards AFB CA 93523.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) High Density Nitric Acids      Vapor Pressure Density      Corrosion Product Solubility Specific Gravity      Passivation		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Two techniques were employed to determine the density of Modified HDA (High Density Acid), a blend of nitric acid and nitrogen dioxide, containing phosphorous pentafluoride as a corrosion inhibitor. Reliable data were obtained by use of pycnometers. Errors found by use of hydrometers were of a magnitude sufficient to affect subsequent rocket engine performance calculations. A two-cube factorial experiment was performed to determine which component(s) of Modified HDA control vapor pressure. Nitrogen dioxide was found to be the principal controlling variable. The experiment also provided accurate data for total (equilibrium) pressure as a function of temperature.		

054051



ACCE. N  
N IS  
D.C.  
FY  
B

**SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)**

## SUMMARY

Previous studies have proven that HDA (High Density Acid), a blend of nitric acid and nitrogen dioxide, is less corrosive to metals in Agena propulsion systems when phosphorous pentafluoride is substituted for hydrofluoric acid as the corrosion inhibitor. The blend containing hydrofluoric acid is referred to as Standard HDA. The blend containing phosphorous pentafluoride is referred to as Modified HDA. The tests described in this report were performed to better characterize Modified HDA in terms of select physical properties and the formation and solubility of corrosion products. The physical properties measured were density, specific gravity and vapor pressure. Solubility tests included not only Modified HDA but also Standard HDA.

The density of Modified HDA was measured, using a pycnometer constructed of compatible materials, and calculated from specific gravity readings, obtained by use of a hydrometer. Nine blends of Modified HDA, representing systematic variations in nitrogen dioxide and water content, were subjected to pycnometric measurements as a function of temperature. A portion of each blend was then subjected to a specific gravity measurement at a common temperature of 60°F (15.6°C). A regular increase in density was found pycnometrically for each blend with a decrease in temperature. The values for density calculated from specific gravity were higher for the blends than were the values measured with a pycnometer. Relatively small, uniform changes in density at a constant temperature and water content were found pycnometrically depending on the nitrogen dioxide content of a given blend. Density was highest for blends containing 44 weight percent nitrogen dioxide. Density at constant temperature and constant nitrogen dioxide content increased drastically with decreasing water content. Variations in specific gravity readings were random. These variations are referred to as "buoyancy effects" associated with hydrometers. These effects can introduce errors of 0.3% in density readings. Errors of this magnitude would bias rocket engine performance calculations based on weight flows calculated from hydrometer readings. For this reason, the use of hydrometers is discouraged. The curves for density of the blends studied as a function of temperature proved to be linear, and parallel, with a slope of -0.0020 grams/cubic centimeter/degree Celsius. Density determined pycnometrically at a convenient temperature can be extrapolated to another temperature over the range studied, from the slope of the curves. This procedure is recommended for routine measurements employing a pycnometer developed for the purpose. Close agreement exists between the slope of the curves for Modified HDA and data in the literature for Standard HDA and unmodified HDA. Additional pycnometric measurements should be performed to obtain accurate data concerning changes in the density of Standard HDA as functions of temperature and composition.

A two cube factorial experiment was conducted to determine which of the constituents of Modified HDA control vapor pressure. The experiment involved measurements with eight blends of acid with carefully adjusted concentrations of nitrogen dioxide, water and phosphorous pentafluoride. Each blend was subjected to measurements of pressure and temperature at constant volume. An increase in temperature for any given blend was accompanied by an increase in pressure. Increasing the phosphorous pentafluoride concentration had a negligible effect on pressure at a given temperature. A larger effect was associated with an increase in water content. Nitrogen dioxide, however, proved to be an unmistakable controlling variable. An increase in nitrogen dioxide content by as little as one percent by weight caused a measureable increase in pressure.

The vapor pressure experiment was further designed to test the effect of increasing ullage. For a given blend, an increase in ullage resulted in a decrease in pressure. This decrease was related

to a decomposition pressure component, as well as a vapor pressure component, for the total pressure measured, when the system was at equilibrium under a given set of conditions. The vapor pressure component was proven to be due principally to nitrogen dioxide in the vapor phase. The decomposition pressure component was related to the presence of a relatively small amount of oxygen. Calculations based on the experimental data indicated that decomposition pressure accounted for approximately 3% of the equilibrium pressure measured. This increment should be deducted from reported, total pressures, to arrive at more accurate inlet conditions for turbine pump design. Propellant tank designs must consider the total equilibrium pressure.

Data in the literature suggest similar trends to those above concerning the vapor pressure of Standard HDA. Measurements of the type performed during this program are needed to define the system more precisely. An improvement in the method for determining nitrogen dioxide content of the acid being studied would be advantageous.

Systematic measurements of the solubility of corrosion products in Modified HDA were performed to allow more precise prediction of the service life of a given propellant blend, at a given temperature, before plugging of propulsion system filters is likely to occur. The studies involved filtration of a given blend, at a given temperature, and pre and post test analyses of the acid for concentrations of specific metals. The corrosion products had formed through reactions between Modified HDA and aluminum alloys and stainless steels. The tests were repeated with portions of the acids fortified by addition of more nitrogen dioxides or water. Finally, each blend was filtered at a reduced temperature. Limited comparisons were made with Standard HDA. The effects of changing nitrogen dioxide and water contents and decreasing temperature were negligible.

The solubility tests proved that prior treatment of the metal being corroded, the amount of ullage, and the corrosion inhibitor are critical factors. HDA tends to dissolve and become contaminated with pre-existent films. High ullage promotes formation of relatively insoluble oxides. Metal salts formed by combinations with corrosion inhibitor anions tend to be less soluble than the corresponding, and more prevalent, nitrates. Common ion effects reduce the solubility of any given species. These effects are more pronounced with respect to the anion than the cation. Particles precipitate when the solubility product of a given species is exceeded. The highly colored nature of the solvent makes visual detection difficult, but visual inspections, combined with chemical analyses, proved that the solubility of corrosion products is virtually the same in Modified and Standard HDA. Further tests with more highly contaminated solutions, and solubility tests with select, pure solutes, are needed for more precise differentiation.

Since Standard HDA is more corrosive than Modified HDA, it was postulated and proven that particles are observed more quickly when Standard HDA is exposed to a given metal, than when exposure is to Modified HDA. Stainless steel and aluminum corrosion products formed during attempts to passivate metal combinations of the types in the Agena oxidizer tank sump, on short term exposure of test specimens to Modified HDA. Maximum test duration was 28 days. Corrosion began after a well marked induction period, and continued at a relatively constant rate, with no evidence of passivation. The solubility of none of the corrosion products was exceeded. In contrast, the solubility of stainless steel corrosion products in Standard HDA, was exceeded within one week. The acid appeared clear, and there were no deposits visible on the test specimens. Corrosion continued at a relatively constant rate for the duration of the test. By the end of the test, particles were visible in the acid, but the test specimens were clean. There was no evidence of anodic protection of components of couples of stainless steel and aluminum alloy included in the test matrices.

The behavior of metal/propellant combinations, noted during the passivation tests with Modified HDA, argues against a theory that corrosion is controlled by saturation of the acid with a given species of corrosion products. The facts observed are more consistent with a theory of protective film formation. Data from other tests with Modified HDA are presented in support of the latter theory. Additional tests of the same type are needed to extend the film protection theory with equal conviction to Standard HDA. Review of data from pertinent tests being conducted at the University of Nottingham may effect this objective.



## CONTENTS

Section	Page
I INTRODUCTION .....	8
II TECHNICAL DETAILS .....	9
1.0 Task 1 - Characterization of Modified HDA .....	9
1.1 Density .....	9
1.2 Specific Gravity and Buoyancy Effects .....	17
1.3 Vapor Pressure .....	22
2.0 Task 2 - Solubility Tests .....	57
2.1 Corrosion Product Solubility Tests .....	57
2.2 Passivation Tests .....	70
III TECHNICAL DISCUSSION .....	98
1.0 Task 1 - Characterization of Modified HDA .....	98
1.1 Density .....	98
1.2 Specific Gravity and Buoyancy Effects .....	100
1.3 Vapor Pressure .....	101
2.0 Task 2 - Solubility Tests .....	112
2.1 Corrosion Product Solubility Tests .....	112
2.2 Passivation Tests .....	126
IV CONCLUSIONS AND RECOMMENDATIONS .....	145
1.0 Conclusions .....	145
2.0 Recommendations .....	146
V REFERENCES .....	148
VI LIST OF ABBREVIATIONS AND SYMBOLS .....	149

## ILLUSTRATIONS

Figure		Page
1	Pycnometers .....	10
2	Sample Density Calculation .....	12
3	Modified HDA Density ..	20
4	Sample Specific Gravity Calculation .....	22
5	Vapor Pressure Test Vessels .....	24
6	Calibration and Vapor Pressure Test Vessels .....	26
7	Vapor Pressure Test Equipment .....	28
8	Vapor Pressure Experiment .....	35
9	Vapor Pressure Run, Stock Solution 1 .....	47
10	Vapor Pressure Run, Stock Solution 2 .....	49
11	Vapor Pressure Run, Stock Solution 3 .....	50
12	Vapor Pressure Run, Stock Solution 4 .....	51
13	Vapor Pressure Run, Stock Solution 5 .....	52
14	Vapor Pressure Run, Stock Solution 6 .....	53
15	Vapor Pressure Run, Stock Solution 7 .....	54
16	Vapor Pressure Run, Stock Solution 8 .....	55
17	HDA Filtration Equipment .....	58
18	Passivation Test Specimens .....	72
19	Passivation Test Vessel .....	74
20	Passivation Test Results - Weight Change - Metals .....	79
21	Passivation Test Results - Corrosion Rate - Aluminum Alloy .....	81
22	Passivation Test Results - Corrosion Rate - Stainless Steel .....	84
23	Passivation Tests - Iron Buildup In Solution .....	89
24	Passivation Tests - Chromium Buildup In Solution .....	92
25	Passivation Tests - Nickel Buildup In Solution .....	94
26	Passivation Tests - Aluminum Buildup In Solution .....	96
27	Vapor Pressure as a Function of $\text{NO}_2$ Content at High Ullage .....	102
28	Vapor Pressure of Modified HDA Compared to Standard HDA .....	104
29	Vapor Pressure of Modified HDA as a Function of $\text{NO}_2$ Content .....	108
30	Vapor Pressure of Modified HDA as Functions of $\text{H}_2\text{O}$ and $\text{PF}_3$ Contents. ....	109
31	Equilibrium Pressure Calculations .....	110
32	Solubility of Aluminum Salts in Modified HDA .....	122
33	Prediction of Passivation Test Results .....	128
34	Passivation Test Calculations .....	133
35	Saturation Limit Calculations .....	135
36	Iron Buildup in Solution as a Function of S/V Ratio .....	140

## TABLES

Number		Page
1	Pycnometer Calibration Data . . . . .	11
2	Stock Solutions - Density, Specific Gravity and Buoyancy Determinations . . .	11
3	Test Matrix for Modified HDA Density Determinations . . . . .	13
4	Modified HDA Density . . . . .	14
5	Chemical Analyses Supporting Density Determinations . . . . .	18
6	Modified HDA Specific Gravity and Buoyancy Effects . . . . .	21
7	Vapor Pressure Test Matrix . . . . .	23
8	Vapor Pressure Calibration Data . . . . .	27
9	Vapor Pressure Experiments . . . . .	30
10	Decomposition Pressure - Experiment 1 . . . . .	36
11	Nitrogen Dioxide Losses . . . . .	37
12	Nominal Concentrations of Vapor Pressure Stock Solutions . . . . .	37
13	Vapor Pressure Runs . . . . .	38
14	Modified HDA Pressure Versus Temperature at Constant Volume . . . . .	56
15	Modified HDA Pressure Versus Volume at Constant Temperature . . . . .	56
16	Preliminary Solubility Tests - Filter Compatibility . . . . .	59
17	Pure Stock Solutions for Solubility Tests . . . . .	59
18	Preliminary Solubility Tests - Filter Membrane Selection . . . . .	60
19	Corrosion Product Solubility Tests - Series 1 . . . . .	63
20	Corrosion Product Solubility Tests - Series 2 . . . . .	68
21	Corrosion Product Solubility Tests - Series 3 . . . . .	69
22	Passivation Test Log . . . . .	75
23	Passivation Test Parameters . . . . .	76
24	Passivation Test Data . . . . .	77
25	Passivation Test Results - Metals . . . . .	78
26	Passivation Test Results - Acids . . . . .	86
27	Slope of HDA Density Curves . . . . .	99
28	HDA Density as a Function of Corrosion Inhibitor . . . . .	100
29	NO <sub>2</sub> Loss on Expansion . . . . .	105
30	Calculated Pressure of Vapors Upon Expansion . . . . .	106
31	Pressure Drops Due to Expansion . . . . .	106
32	Miscellaneous, Room Temperature Solubility Tests . . . . .	112
33	Preliminary, Room Temperature Solubility Test Data . . . . .	114
34	Accuracy of Solubility Test Analyses . . . . .	115
35	Standard HDA Corrosion Product Solubility Tests . . . . .	116
36	Modified HDA Corrosion Product Solubility Tests - Series 1 . . . . .	118
37	Modified HDA Corrosion Product Solubility Tests - Series 2 and 3 . . . . .	119
38	Modified HDA Corrosion Product Solubility Tests - Series 3 . . . . .	120
39	Solubility of Corrosion Product Films . . . . .	123
40	Current, Room Temperature Solubility Test Data . . . . .	125
41	Corrosion Test Results - 304 SS Cloth/6061-O-W . . . . .	129
42	Compatibility Classification of Materials with Rocket Propellants . . . . .	130
43	Standard HDA Passivation Kinetics . . . . .	132
44	Corrosion Rates of Components and Couples . . . . .	134
45	Corrosion Product Solubility Data from Passivation Test Data . . . . .	136
46	Anodic Protection During Passivation Tests of Couples . . . . .	138
47	Acids for Tests of Corrosion Control Mechanisms . . . . .	141
48	Compatibility Test Results . . . . .	142
49	Composition of Films on Test Tanks for Modified HDA . . . . .	143
50	Thickness of Films on Test Tanks for Modified HDA . . . . .	144

## I. INTRODUCTION

The Agena propulsion system has been in operation since 1957. To date, several engine modifications and propellant changes have been made to increase performance. Notable among the latter was a change from Inhibited Red Fuming Nitric Acid to Standard High Density Acid. Hydrogen fluoride is added to both of these oxidizers as a corrosion inhibitor. Experience proved hydrogen fluoride to be less effective in High Density Acid (HDA), and a search was instituted for a corrosion inhibitor which would extend the useful life of the oxidizer.

Under Contract F04611-72-C-0026 Bell Aerospace Textron developed a superior corrosion inhibitor, phosphorous pentafluoride which promised long term storability and extended mission life. The new oxidizer was named Modified HDA. Extended storage tests completed under Contract F04611-73-C-0069 showed that the new oxidizer could be stored for two years in aluminum and stainless steel tanks with insignificant corrosion.

Under Contract F04611-76-C-0054 the corrosiveness of Standard HDA and Modified HDA toward a variety of materials in Agena and ISPS (Integrated Secondary Propulsion System) engines was compared. Modified HDA was found to be significantly less corrosive than Standard HDA. Additional data were obtained concerning the analysis and some of the properties of the two acids. There was no significant effect on substitution of one corrosion inhibitor for the other.

The principal objective of the work described in this report was the precise determination of the density and vapor pressure of Modified HDA as functions of temperature and composition of the acid. Additional data were obtained concerning the solubility of corrosion products in a given acid, and the tendency of metals exposed to the acids to become passive with time. Results of the work performed are included in the body of the report.

A list of frequently used abbreviations and symbols is provided at the end of the report.

## II. TECHNICAL DETAILS

### 1.0 TASK 1 - CHARACTERIZATION OF MODIFIED HDA

#### 1.1 Density

A set of experiments was conducted with the object of measuring the density of Modified HDA as functions of temperature and composition in inert equipment designed to provide data in basic units (mass and volume). This was accomplished by constructing two pycnometers, each with an aluminum bottle and an indexed, synthetic sapphire capillary. The pycnometers were filled with a given acid and held in a constant bath until thermal equilibrium was established, as indicated by no further rise of acid into the capillary.

The design of the pycnometers is illustrated in Figure 1. In addition to a bottle and a capillary, each unit included a protective sheath with engraved marks to serve as indices for the enclosed capillary, a ball valve for loading and containing the acid sample, fittings for attaching the sheath to the bottle at one end and the valve at the other, and Teflon glands inside the fittings to prevent leakage around the capillary. The bottle and valve of one assembly were marked A/A and the other B/B, so that parts would not be interchanged after calibration.

The pycnometers were calibrated with distilled water, using a large capacity balance to measure mass and a cathetometer to read the elevation of liquid in the capillary. The total volume of each pycnometer was determined from weighings after evacuation and when the pycnometer was full of water at constant temperature. The volume to the lower index mark was determined by monitoring the rise of liquid with increasing temperature after each pycnometer was partially filled with water under vacuum. Different amounts of water were added in separate trials to allow calculations of the changes in volume of the bottles with temperature. Data at higher temperatures were used to calculate the volumes of the capillaries per unit length. The results of the calibration steps are summarized in Table 1.

Nine batches of Modified HDA containing three levels of nitrogen dioxide content and three levels of water content were prepared and analyzed by standard procedures (Reference 1<sup>a</sup>). The composition of the acids is given in Table 2. No water was deliberately added to the first three blends. The variations in water content reflect minor differences in the starting materials. Calculated amounts of water were added prior to nitrogen dioxide addition during preparation of the other blends. Large enough batches were prepared in each case so that density and specific gravity measurements could be made on portions of the same stock solution.

Measurement of the density of each stock solution as a function of temperature began by filling the pycnometer bottle to overflowing with chilled acid, attaching the superstructure (capillary, sheath, etc.) with the valve open, closing the valve, cleaning off excess acid, and weighing the assembly after the acid reached room temperature. The assembly was then suspended, by a clamp around the top of the valve, in a clear, constant temperature water bath. The rise of acid into the capillary was monitored with a cathetometer, using techniques described in Reference 1. When thermal equilibrium was reached, as judged by no further movement of the acid, the height of the meniscus above the lower capillary index was measured. The temperature of the bath was then

---

<sup>a</sup>Reference 1. "Agena/ISPS Component Compatibility Study," H. Ph. Heubusch, Bell Aerospace Textron, AFRPL-TR-78-10, March 1978.

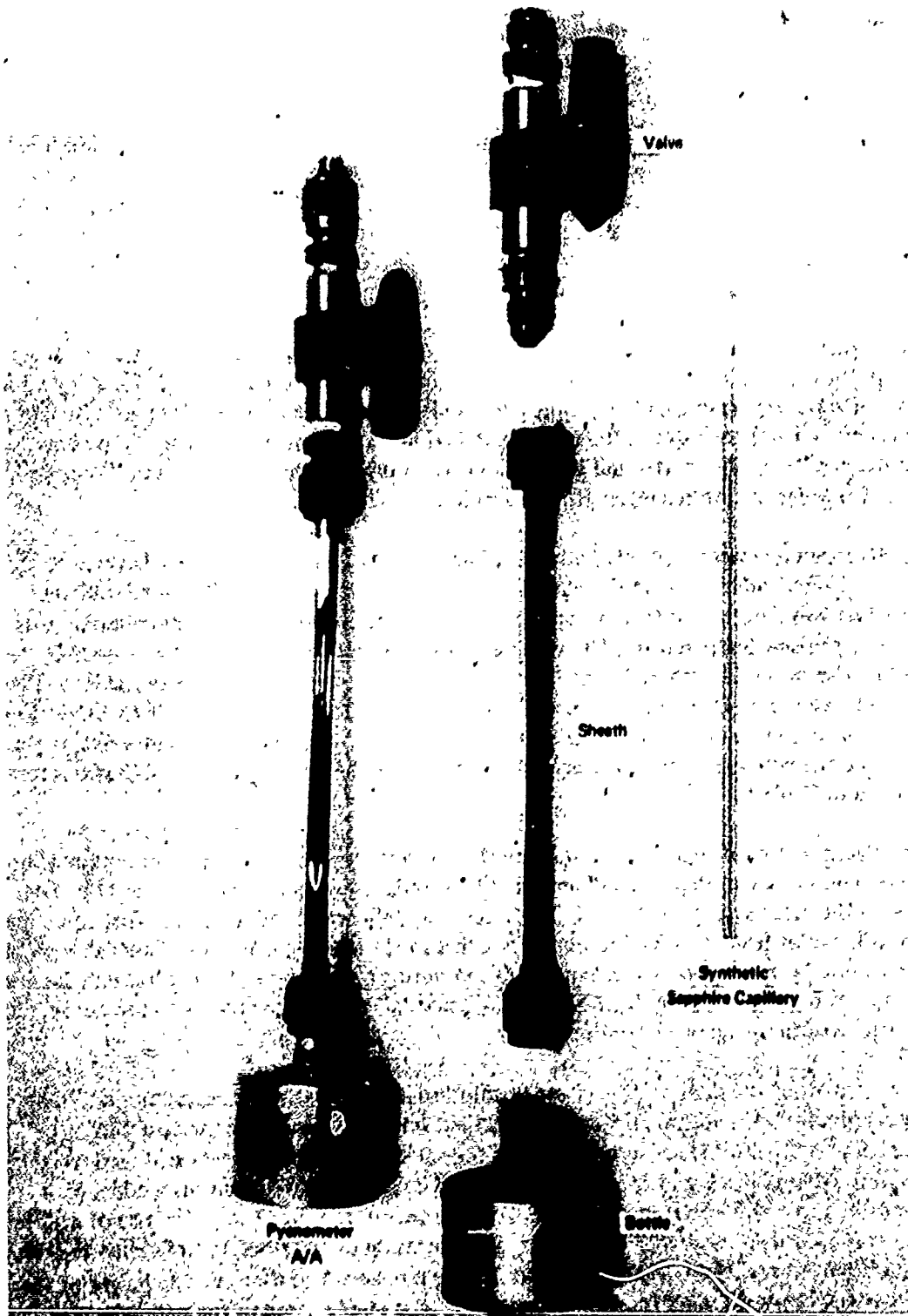


Figure 1. Pycnometers

TABLE 1. PYCNOMETER CALIBRATION DATA

Item	Pycnometer A/A	Pycnometer B/B
Weight, gm	128.5015	138.7908
Weight, Evacuated, gm	128.4516	138.7142
Total Volume @ 20°C (68°F), cm <sup>3</sup>	30.7592	37.9544
Volume to Lower Index Mark, cm <sup>3</sup>		
@ 20.1°C (68.1°F)	29.9590	36.6588
@ 26.7°C (80.0°F)	29.9840	36.8844
Δ cm <sup>3</sup> /°C	0.00379	0.00388
Volume of Capillary, cm <sup>3</sup> /cm	0.01900	0.01900

TABLE 2 STOCK SOLUTIONS  
DENSITY, SPECIFIC GRAVITY AND BUOYANCY DETERMINATIONS

Stock No.	Physical Appearance	wt %						ppm (w/w)		
		HNO <sub>3</sub>	NO <sub>2</sub>	H <sub>2</sub> O	PF <sub>5</sub>	Fe <sub>2</sub> O <sub>3</sub>	M <sub>2</sub> O <sub>3</sub>	Cr	Ni	Al
77-15	Clear	Bal.	42.1	0.1	0.5	0.0002	0.0007	<1.0	<1.0	<1.0
77-07	Clear	Bal.	44.2	0.2	0.5	0.0001	0.0002	<1.0	<1.0	<1.0
77-08	Clear	Bal.	46.0	0.1	0.5	0.0002	0.0002	<1.0	<1.0	<1.0
77-09	Clear	Bal.	42.4	0.5	0.5	0.0003	0.0005	<1.0	1.0	<1.0
77-10	Clear	Bal.	44.3	0.5	0.5	0.0003	0.0005	<1.0	1.0	<1.0
77-11	Clear	Bal.	46.1	0.5	0.5	0.0005	0.0005	<1.0	1.0	<1.0
77-12	Clear	Bal.	42.1	1.0	0.5	0.0003	0.0006	<1.0	1.0	<1.0
77-13	Clear	Bal.	44.2	1.0	0.5	0.0002	0.0003	<1.0	1.0	<1.0
77-14	Clear	Bal.	46.2	1.0	0.5	0.0003	0.0008	<1.0	1.0	<1.0

changed and the process repeated. The density of the acid at each temperature was determined from the weight of the acid and its volume, as calculated from cathetometer readings and calibration factors. A sample calculation is given in Figure 2. After the test, the assembly was removed from the constant temperature bath, dried and reweighed. The superstructure was removed and samples of acid were drawn and analyzed.

In addition to the standard procedure just described, three variations were employed. In the simplest case, the same stock solution was examined separately, by the standard procedure, in each pycnometer. A second variation consisted of underfilling the bottle so that data could be obtained at relatively high temperatures before the meniscus of the acid rose out of the field of view. The third variation consisted of loading the same stock solution in each pycnometer, then chilling the acid and evacuating the capillary, before immersing the pycnometers in the constant temperature bath. Since the pycnometer bottles were of different size, the resulting data could be used to calculate the orthobaric density of the liquid as well as the density of the acid's vapors. The complete test matrix is shown in Table 3. It will be noted that Run No. 2 with acid Stock No. 77-12 was aborted. This was done because too little acid had been loaded to give data in the standard temperature range.

Table 4 contains the results of density calculations for each experimental point taken. Data are arranged by nominal composition of the stock solutions, not in the order in which the solutions

$$\begin{aligned}
 &\text{Stock No. 77-15 (42 wt\% NO}_2\text{) in Pycnometer A/A} \\
 T^\circ &= 15.28^\circ\text{C (59.5}^\circ\text{F)} \\
 \text{gm} &= 177.8113 \text{ gm Pycnometer + Modified HDA} \\
 &\quad - 128.4165 \text{ gm Pycnometer} \\
 &\quad \underline{49.3948 \text{ gm Modified HDA}} \\
 h &= 83.710 - 82.645 = 1.065 \text{ cm} \\
 &= \text{height of acid in capillary above lower reference} \\
 &\quad \text{mark on sheath} \\
 v_{20.1^\circ} &= \text{volume of pycnometer to lower} \\
 &\quad \text{reference mark at } 20.1^\circ\text{C} = 29.9590 \text{ cm}^3 \\
 v_{15.3^\circ} &= (0.00379) (15.3 - 20.1) = -0.0182 \text{ cm}^3 \\
 &= \text{temperature correction (cm}^3\text{/}^\circ\text{C) for} \\
 &\quad \text{contraction of bottle on cooling} \\
 \text{Cap.} &= 0.019 \times 1.065 = 0.0202 \text{ cm}^3 \\
 &= \text{volume of acid in capillary above} \\
 &\quad \text{lower reference mark on sheath} \\
 \text{vol} &= \text{total volume of acid at } T^\circ \quad \underline{29.9610 \text{ cm}^3} \\
 \rho_{15.28^\circ} &= \frac{49.3948 \text{ gm}}{29.9610 \text{ cm}^3} = 1.6486 \text{ gm/cm}^3 \text{ at } 15.28^\circ\text{C}
 \end{aligned}$$

Figure 2. Sample Density Calculation

were studied. For each stock solution, however, data are presented in the order in which the Runs were made, and include the identification of the pycnometer used and the type of test performed. For each Run, density data are presented in the order of increasing temperature. When data at a given temperature were derived in different ways, the point is made in a column of comments. Some of the comments are self-explanatory. Some will be considered in Part III, Technical Discussion. Those comments related to test procedures will now be explained.

The lubricant, Krytox, was applied lightly to the lower fitting of pycnometer A/A before Run No. 2 with stock solution 77-13, after the packing gland cracked during the first Run, and had to be replaced. The lubricant was left in place for Run No. 2 with stock solution 77-13 and Run No. 1 with stock solution 77-15. After the last named Run, the filled assembly was reweighed to confirm that no weight change had occurred during test. The pycnometer was subsequently emptied and reweighed after the Krytox had been removed. The differences in density calculated for each case were negligibly small, but the practice of using Krytox was discontinued as a precautionary measure.

On the average, the data for Run No. 2 with stock solution 77-7 were acceptable, but the deviation between experimental points was relatively large. Similar deviations were noted for Run No. 1 with stock solution 77-12 and Run No. 2 with stock solution 77-14. In the former case an attempt was made to use an air bath rather than a constant temperature water bath. In each case, cathetometer readings were taken before thermal equilibrium had been established.



TABLE 3. TEST MATRIX FOR MODIFIED HDA DENSITY DETERMINATIONS

Stock No.	Acid Composition		Type Measurement	Run No.	Pycnometer	Temperature Range		Comments
	wt% NO <sub>2</sub>	wt% H <sub>2</sub> O				°C	°F	
77-15	42	0.1	Standard	1	A/A	15.28 - 17.00	59.5 - 62.6	Aborted.
77-7	44	0.2	Standard	1	B/B	12.06 - 14.61	53.7 - 58.3	
				2	B/B	16.11 - 17.00	61.0 - 62.6	
77-8	46	0.1	Standard	1	B/B	12.78 - 15.39	55.0 - 59.7	
77-9	42	0.5	Standard	1	B/B	12.78 - 15.56	55.0 - 60.0	
77-10	44	0.5	Standard	1	A/A	15.83 - 19.50	60.5 - 67.1	
				2	A/A	13.94 - 15.56	57.1 - 60.0	
				3	B/B	15.00 - 16.06	59.0 - 60.9	
				1	A/A	22.67 - 30.89	72.8 - 87.6	
				2	B/B	28.11 - 30.89	82.6 - 87.6	
			Orthobaric	1	A/A, B/B	20.39 - 21.33	68.7 - 70.4	
77-11	46	0.5	Standard	1	B/B	13.33 - 16.00	56.0 - 60.8	
77-12	42	1.0	Standard	1	B/B	22.89 - 28.11	73.2 - 82.6	
				2	B/B	-	-	
				3	B/B	17.22 - 19.78	63.0 - 67.6	
77-13	44	1.0	Standard	1	A/A	13.89 - 15.61	57.0 - 60.1	
				2	A/A	12.78 - 14.61	55.0 - 58.3	
				3	A/A	16.17 - 16.22	61.1 - 61.2	
77-14	46	1.0	Standard	1	A/A	-	-	
				2	B/B	14.72 - 15.61	58.5 - 60.1	
				3	A/A	17.22 - 18.11	63.0 - 64.6	

Sodium dichromate was added to the constant temperature water bath to inhibit corrosion of the aluminum pycnometer bottles. On occasion, as for example after Run No. 1 with stock solution 77-8, stains were noted on the bottle when it was removed from the water bath. On such occasions, the pycnometer was reweighed before and after removing the stains with a solution of nitric and hydrofluoric acids. The operation had a negligible effect on results.

As indicated above, a Teflon gland on the pycnometer used for Run No. 1 with stock solution 10 cracked during the Run. A leak developed and invalidated subsequent test points. After the third Run with this acid, the assembly was returned to the water bath and allowed to stand for approximately three days. When reweighed, no measurable change was detected. The same was found true for the other pycnometer in a similar experiment conducted after Run No. 3 with stock solution 77-13. These experiments were performed in preparation for long duration, high temperature and orthobaric density measurements.

Stock solution 77-10 was used for the long duration tests. In all cases, bubbles appeared in the capillaries during the tests. After the tests, significant changes were noted in the weights of the assemblies. Taken together, these facts make the experimental data unreliable. It appears that air was trapped in the bottles during filling and leaks developed during the tests.

TABLE 4. MODIFIED HDA DENSITY (1 of 3)

Sheet No.	wt %		Type Test	Run No.	Pyc ID	Temperature		Density, gm/cm <sup>3</sup>	Comments
	KNO <sub>3</sub>	H <sub>2</sub> O				°C	°F		
77-15	42	0.1	Standard	1	A/A	15.28	59.5	1.8486	Curve 9, Figure 3.
						15.83	60.5	1.8476	
						16.11	61.0	1.8472	
						16.17	61.1	1.8470	
						17.00	62.6	1.8456	
						15.83	60.5	1.8476	
77-7	44	0.2	Standard	1	B/B	15.83	60.5	1.8477	Pre Test Weight. Post Test Weight. After Krytox Removed. Curve 7, Figure 3.
						15.83	60.5	1.8478	
						12.06	53.7	1.8483	
						13.33	56.0	1.8467	
						14.11	57.4	1.8454	
						14.61	58.3	1.8446	
77-8	46	0.1	Standard	2	B/B	16.11	61.0	1.8397	Data Unreliable, Thermal Lag. Data Unreliable, Thermal Lag. Curve 8, Figure 3.
						17.00	62.6	1.8421	
						12.78	55.0	1.8504	
						13.33	56.0	1.8498	
						13.94	57.1	1.8484	
						15.39	59.7	1.8457	
						15.39	59.7	1.8456	After Stains Removed.

TABLE 4. MODIFIED HDA DENSITY (2 of 3)

Stock No.	wt %		Type Test	Run No.	Pyc ID	Temperature		Density gm/cm <sup>3</sup>	Comments
	NO <sub>2</sub>	H <sub>2</sub> O				°C	°F		
77-9	42	0.5	Standard	1	E/B	12.78	55.0	1.6432	Curve 5, Figure 3.
						13.67	56.6	1.6416	
						14.17	57.5	1.6407	
						15.50	60.0	1.6382	
77-10	44	0.5	Standard	1	A/A	15.83	60.5	1.6378	Curve 6, Figure 3
						16.00	60.8	1.6377	
						16.67	62.0	1.6372	
						16.72	62.1	1.6375	
						12.78	55.0	1.6435	
						13.94	57.1	1.6414	
						15.67	60.2	1.6385	
						15.00	59.0	1.6391	
						16.06	60.9	1.6372	
						16.00	60.9	1.6372	
77-11	46	0.5	Orthobaric	1	A/A	22.67	72.8	1.6131	Data Unreliable, Bubbles.
						24.11	75.4	1.6112	
						28.11	82.6	1.6128	
						29.17	84.5	1.6106	
						30.11	86.2	1.6089	
						30.89	87.6	1.6075	
						30.89	87.6	1.6058	
						28.11	82.6	1.6115	
						29.17	84.5	1.6094	
						30.11	86.2	1.6077	
						30.89	87.6	1.6062	
						30.89	87.6	1.6044	
						20.39	68.7	1.6170	
						20.39	68.7	0.4354	
77-11	46	0.5	Standard	1	B/B	21.33	70.4	1.6159	Vapor, Data Unreliable, Ibid.
						13.28	55.9	1.6389	
						14.00	57.2	1.6378	
						15.50	59.9	1.6352	
77-11	46	0.5	Standard	1	B/B	16.00	60.8	1.6342	Curve 4, Figure 3.

TABLE 4. MODIFIED HDA DENSITY (3 of 3)

Stack No.	wt %		Type Test	Run No.	Pyc ID	Temperature		Density, gm/cm <sup>3</sup>	Comments
	NO <sub>2</sub>	H <sub>2</sub> O				°C	°F		
77-12	42	1.0	Standard	1	B/B	22.89	73.2	1.6128	Air Bath, Data Unreliable. Water Bath. Curve 1, Figure 3.  Aborted, Underfilled.    Data Unreliable, Leak. ibid. ibid. ibid. Curve 3, Figure 3.  After 67 Hour Hold. Aborted, Underfilled. Data Unreliable, Thermal Lag. Curve 2, Figure 3. Data Unreliable. Data Unreliable. Changed Pycnometers.
						25.22	77.4	1.6135	
						26.44	79.6	1.6095	
						28.11	82.6	1.6081	
						-	-	-	
						17.22	63.0	1.6291	
						18.61	65.5	1.6286	
						19.17	66.5	1.6264	
						19.78	67.6	1.6245	
						13.89	57.0	1.6390	
77-13	44	1.0	Standard	1	A/A	14.56	58.2	1.6375	
						15.61	60.1	1.6341	
						16.56	61.8	1.6331	
						12.78	55.0	1.6394	
						13.94	57.1	1.6372	
						14.61	58.3	1.6359	
						16.17	61.1	1.6325	
						16.22	61.2	1.6323	
						16.17	61.1	1.6323	
						-	-	-	
77-14	46	1.0	Standard	1	A/A	14.72	58.5	1.6326	
						15.61	60.1	1.6336	
						16.11	61.0	1.6348	
						17.72	63.9	1.6339	
						17.22	63.0	1.6299	
						18.11	64.6	1.6284	
						-	-	-	
				2	B/B	14.72	58.5	1.6326	
						15.61	60.1	1.6336	
						16.11	61.0	1.6348	
				3	A/A	17.72	63.9	1.6339	
						17.22	63.0	1.6299	
						18.11	64.6	1.6284	

As previously indicated, Run No. 2 with stock solution 77-12 was aborted when it was discovered that too little acid had been loaded to bring the liquid into view in the desired temperature range. Run No. 1 with stock solution 77-14 was aborted for the same reason.

Table 5 contains the results from chemical analysis made in support of density and subsequent specific gravity determinations. Continuity with Tables 2-4 is provided by acid Stock Number and pertinent comments. The first entry for each Run is the analysis for the stock solution completed the day the pycnometer was loaded. The next entry is a partial analysis made on acid removed from the pycnometer after the test. The appearance of the acid and its aluminum content were determined as checks on corrosion of metal pycnometer parts. Nitrogen dioxide and water contents were determined as checks for leaks. Subsequent entries in the table are for successive Runs with the same stock solution and/or analyses made in support of the specific gravity measurements. In the latter case, no analyses for metals were warranted. Two sets of post test analyses are shown for the orthobaric density test with stock solution 77-10, because two pycnometers were used for this test. Water contents determined in support of orthobaric and high temperature tests are shown to the hundredth percent in Table 5 to emphasize the point that leaks developed during these tests. Satisfactory results of post test analyses for a density determination were the normal signal to make a specific gravity determination. In one case, Run No. 1 with stock solution 77-13, an error in pycnometer weights was found after the specific gravity determination had been made on the basis of satisfactory post-density chemical analyses. In two cases, Run No. 1 with stock solution 77-12 and Run No. 1 with stock solution No. 14, post test analyses were not completed because the runs had been aborted.

Plots of the density of each stock solution, as a function of temperature, over the range covered by the standard test technique, are shown in Figure 3. Points were taken from the most reliable data in Table 4. The curves have been numbered in the order of their appearance from left to right. The nominal percentage of nitrogen dioxide in each case is shown with the curve number. Nitrogen dioxide content is also distinguished by the symbols used for the data points. The symbols, the nominal composition of each blend and the acid Stock No. are given in the Legend of the graph.

It is immediately evident that the curves have the same slope, allowing extrapolation from one temperature to another within the limits of the graph. Interpolation between curves is less reliable. The curves fall in three families with three different water contents. Density at a given temperature, for a given nitrogen dioxide content, increases with a decrease in water content. Maximum density, at a given temperature and water content, is associated with blends containing 44 wt % (weight percent) nitrogen dioxide. Further generalizations are given in Part III, Technical Discussion.

## 1.2 Specific Gravity and Buoyancy Effects

A set of tests was conducted with the object of measuring the specific gravity of several samples of modified HDA for which precise density data were available. Specific gravity readings were determined at constant temperature, using a hydrometer. Density had been measured previously, as a function of temperature, with a pycnometer. Density was also calculated from the specific gravity readings. The differences in the density of the acids as determined by the two techniques are defined as the "buoyancy effect" associated with the hydrometer.

The experimental objective was achieved by use of part of the stock solutions employed for density determinations as described in Section 1.1. Before actual density measurements began, several hydrometers were calibrated for sequential measurements of specific gravity. Calibration of the hydrometers involved measurements of the specific gravity of a pseudo Modified HDA whose density had been determined precisely with a conventional glass pycnometer. A blend of phosphoric acid and water, similar in density, at the calibration temperature of 15.56°C (60°F), to Modified HDA,

TABLE 5. CHEMICAL ANALYSES SUPPORTING DENSITY DETERMINATIONS (1 of 2)

Stock No.	Physical Appearance	wt%						ppm (w/w)			Comments
		HNO <sub>3</sub>	NO <sub>2</sub>	H <sub>2</sub> O	PF <sub>5</sub>	Fe <sub>2</sub> O <sub>3</sub>	Mn <sub>2</sub> O <sub>3</sub>	Cr	Ni	Al	
77-15	Clear	Bal.	42.1	0.1	0.5	0.0002	0.0007	<1.0	<1.0	<1.0	Pre-Density Run.
	Clear	-	42.1	0.1	-	-	-	-	-	4.0	Post-Density Run.
	Clear	-	42.3	0.1	-	-	-	-	-	-	Pre-Specific Gravity Run.
	Clear	-	42.0	0.1	-	-	-	-	-	-	Post-Specific Gravity Run.
77-7	Clear	Bal.	44.2	0.2	0.5	0.0001	0.0002	<1.0	<1.0	<1.0	Pre-Density Run 1.
	Clear	-	44.2	0.2	-	-	-	-	-	2.0	Post-Density Run 1.
	Clear	-	44.2	0.2	-	-	-	-	-	<1.0	Pre-Density Run 2.
	Clear	-	44.1	0.2	-	-	-	-	-	2.0	Post-Density Run 2.
	Clear	-	44.2	0.2	-	-	-	-	-	-	Pre-Specific Gravity Run.
	Clear	-	43.9	0.2	-	-	-	-	-	-	Post-Specific Gravity Run.
77-8	Clear	Bal.	46.0	0.1	0.5	0.0002	0.0002	<1.0	<1.0	<1.0	Pre-Density Run.
	Clear	-	45.8	0.1	-	-	-	-	-	3.0	Post-Density Run.
	Clear	-	45.8	0.1	-	-	-	-	-	-	Pre-Specific Gravity Run.
	Clear	-	45.3	0.1	-	-	-	-	-	-	Post-Specific Gravity Run.
77-9	Clear	Bal.	42.4	0.5	0.5	0.0003	0.0010	<1.0	1.0	<1.0	Pre-Density Run.
	Clear	-	42.3	0.5	-	-	-	-	-	2.0	Post-Density Run.
	Clear	-	42.3	0.5	-	-	-	-	-	-	Pre-Specific Gravity Run.
	Clear	-	41.9	0.5	-	-	-	-	-	-	Post-Specific Gravity Run.
77-10	Clear	Bal.	44.3	0.5	0.5	0.0003	0.0005	<1.0	1.0	<1.0	Pre-Density Run 1.
	Clear	-	44.3	0.5	-	-	-	-	-	1.0	Post-Density Run 1.
	Clear	-	44.0	0.5	-	-	-	-	-	<1.0	Pre-Density Run 2.
	Clear	-	44.0	0.5	-	-	-	-	-	3.0	Post-Density Run 2.
	Clear	-	44.2	0.5	-	-	-	-	-	-	Pre-Specific Gravity Run.
	Clear	-	44.0	0.6	-	-	-	-	-	-	Post-Specific Gravity Run.
	Clear	-	44.3	0.5	-	-	-	-	-	<1.0	Pre-Density Run 3.
	Clear	-	44.1	0.5	-	-	-	-	-	2.0	Post-Density Run 3.
	Clear	-	44.3	0.5	-	-	-	-	-	<1.0	Pre-High Temp. Density Run.
	Particles	-	43.9	0.52	-	-	-	-	-	5.0	Post-High Temp. Density Run 1.
	Particles	-	43.9	0.56	-	-	-	-	-	2.0	Post-High Temp. Density Run 2.
	Clear	-	43.9	0.5	-	-	-	-	-	<1.0	Pre-Orthobaric Density Run.
	Particles	-	44.0	0.58	-	-	-	-	-	4.0	Post-Orthobaric Density - A/A.
	Particles	-	43.8	0.54	-	-	-	-	-	2.0	Post Orthobaric Density - B/B.

TABLE 5. CHEMICAL ANALYSES SUPPORTING DENSITY DETERMINATIONS (2 of 2)

Stock No.	Physical Appearance	wt%						ppm (w/w)			Comments
		HNO <sub>3</sub>	NO <sub>2</sub>	H <sub>2</sub> O	PF <sub>5</sub>	Fe <sub>2</sub> O <sub>3</sub>	M <sub>2</sub> O <sub>3</sub>	Cr	Ni	Al	
77-11	Clear	Bal.	46.1	0.5	0.5	0.0005	0.0005	<1.0	1.0	<1.0	Pre-Density Run.
	Clear	-	46.0	0.5	-	-	-	-	-	2.0	Post-Density Run.
	Clear	-	46.0	0.5	-	-	-	-	-	-	Pre-Specific Gravity Run.
	Clear	-	45.5	0.5	-	-	-	-	-	-	Post-Specific Gravity Run.
77-12	Clear	Bal.	42.1	1.0	0.5	0.0003	0.0006	<1.0	1.0	<1.0	Pre-Density Run 1.
	Particles	-	42.2	1.0	-	-	-	-	-	11.0	Post-Density Run 1.
	Clear	-	42.0	-	-	-	-	-	-	-	Pre-Density Run 2.
	-	-	-	-	-	-	-	-	-	-	Run Aborted.
77-13	Clear	-	41.9	1.1	-	-	-	-	-	<1.0	Pre-Density Run 3.
	Clear	-	42.1	1.0	-	-	-	-	-	3.0	Post-Density Run 3.
	Clear	-	41.9	1.0	-	-	-	-	-	-	Pre-Specific Gravity Run.
	Clear	-	41.9	1.0	-	-	-	-	-	-	Post-Specific Gravity Run.
	Clear	Bal	44.2	1.0	0.5	0.0002	0.0003	<1.0	1.0	<1.0	Pre-Density Run 1.
	Clear	-	44.1	1.0	-	-	-	-	-	2.0	Post-Density Run 1.
	Clear	-	44.1	1.0	-	-	-	-	-	-	Pre-Specific Gravity Run 1.
	Clear	-	43.9	1.0	-	-	-	-	-	-	Post-Specific Gravity Run 1.
77-14	Clear	-	44.0	1.0	-	-	-	-	-	<1.0	Pre-Density Run 2.
	Clear	-	43.9	1.0	-	-	-	-	-	2.0	Post-Density Run 2.
	Clear	-	43.9	1.0	-	-	-	-	-	-	Pre-Specific Gravity Run 2.
	Clear	-	43.8	1.0	-	0.0002	-	-	-	-	Post-Specific Gravity Run 2.
	Clear	-	43.8	1.0	-	-	-	-	-	<1.0	Pre-Density Run 3.
	Clear	-	43.6	1.0	-	-	-	-	-	8.0	Post-Density Run 3.
	Clear	Bal.	46.2	1.0	0.5	0.0003	0.0008	<1.0	1.0	<1.0	Pre-Density Run 1.
	Clear	-	-	-	-	-	-	-	-	-	Run Aborted.
	Clear	-	46.2	1.0	-	-	-	-	-	<1.0	Pre-Density Run 2.
	Clear	-	45.9	1.0	-	-	-	-	-	5.0	Post-Density Run 2.
	Clear	-	46.2	1.0	-	-	-	-	-	<1.0	Pre-Density Run 3.
	Particles	-	45.6	1.0	-	-	-	-	-	2.0	Post-Density Run 3.
	Clear	-	46.2	1.0	-	-	-	-	-	-	Pre-Specific Gravity Run.
	Clear	-	45.6	1.0	-	-	-	-	-	-	Post-Specific Gravity Run.

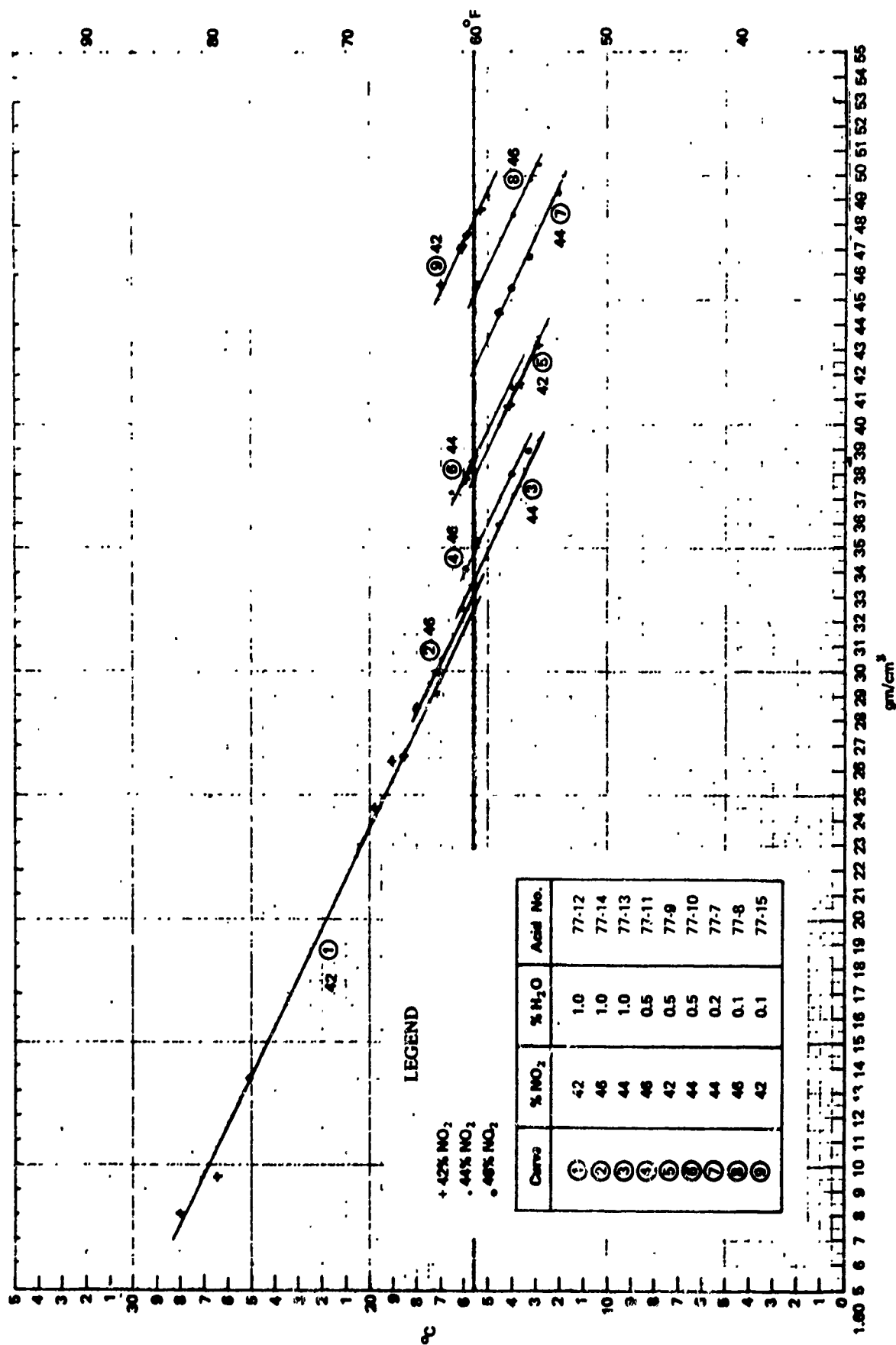


Figure 3. Modified HDA Density



but containing no corrosion inhibitor which would attack the pycnometer, was employed. The constant temperature bath used for density measurements was also used for hydrometer calibrations and specific gravity determinations. Five instruments were compared in search of the hydrometer yielding the closest match to the expected value for the calibration fluid. Hydrometer No. 1219Fh, requiring a correction of -0.0001 units, was selected. This was judged sufficiently accurate for the tests planned. The calibration procedure was repeated after the hydrometer had been used to measure the specific gravity of each stock solution. The correction factor was found to have changed to +0.0001 units, due to etching of the hydrometer by the corrosion inhibitor in Modified HDA. Such a change was anticipated, and proved to be relatively small.

The procedure employed to measure the specific gravity of a given stock solution began with a partial analysis of the stock solution for which satisfactory density data had recently been obtained. The stock solutions were refrigerated between tests and proved to be remarkably stable, based on checks of physical appearance, nitrogen dioxide and water contents. Part of the stock solution, warmed to approximately 14°C (57°F), was poured into a hydrometer jar conditioned to 15.56°C (60°F) in the constant temperature bath. An aluminum cover was installed to minimize loss of nitrogen dioxide during subsequent rise in temperature of the acid, as measured with a stainless steel dial thermometer. When the temperature reached 15.3 °C (59.5°F), the aluminum cover was removed and the hydrometer was lowered into the acid. At 15.56°C (60°F), the specific gravity of the acid was read. The hydrometer was immediately removed and rinsed clean with distilled water. Samples of acid were drawn for inspection and final determinations of nitrogen dioxide and water contents. One spot check was made for pick-up of iron by contact of the acid with the dial thermometer. Refer to Table 5 for the results of all supporting chemical analyses.

The entire process for measuring specific gravity, from insertion to removal of the hydrometer, spanned approximately five minutes. No change in water content was detected between pre and post analyses. Losses of nitrogen dioxide were less than one percent and would affect specific gravity data by less than 0.0005 units. A negligible increase in iron content, less than one part per million (< 1 ppm), was associated with the use of the stainless steel dial thermometer.

The specific gravity for each of the stock solutions examined is shown in Table 6.

TABLE 6. MODIFIED HDA SPECIFIC GRAVITY AND BUOYANCY EFFECTS

Stock No.	wt%		Sp G 60/60°F Corrected gm/cm <sup>3</sup>	Density 60°F Calculated gm/cm <sup>3</sup>	Density 60°F Pycnometer gm/cm <sup>3</sup>	Buoyancy Effect gm/cm <sup>3</sup>	Comments
	NO <sub>2</sub>	H <sub>2</sub> O					
77-15	42	0.1	1.8526	1.8510	1.8482	+0.0028	Hydrometer Readings High.
77-7	44	0.2	1.8491	1.8475	1.8423	+0.0052	
77-8	46	0.1	1.8521	1.8505	1.8451	+0.0054	
77-9	42	0.5	1.8435	1.8419	1.8377	+0.0042	
77-10	44	0.5	1.8425	1.8409	1.8386	+0.0023	
77-11	46	0.5	1.8410	1.8394	1.8348	+0.0046	Similar to 77-12. Rerun.
77-12	42	1.0	1.8364	1.8348	1.8324	+0.0024	
77-13	44	1.0	1.8365	1.8349	1.8336	+0.0013	
77-13	44	1.0	1.8367	1.8351	1.8336	+0.0015	
77-14	46	1.0	1.8369	1.8353	1.8330	+0.0023	

Ten sets of data appear because the specific gravity for stock solution 77-13 was found to be so close to that of stock solution 77-12 that a repeat test was made with stock solution 77-13. Similar

results were obtained for the original and repeat tests. The same trend had been noted for the two acids during the more accurate density determinations. All of the specific gravity data in Table 6 are labeled "corrected" to indicate compensation for changes in hydrometer calibration because of etching during exposure to Modified HDA. The manner in which the reported values were obtained and the maximum effect of etching are shown in the sample calculation, Figure 4. The maximum correction, 0.0002 specific gravity units, is considered to be reasonably small.

Specific Gravity Acid No. 77-15	
Hydrometer No. 1219Fh	
1.6525	Measured Specific Gravity at 60/60°F
-0.0001	Original Calibration Correction
1.6524	Specific Gravity Uncorrected For Etching
1.6525	Measured Specific Gravity at 60/60°F
+0.0001	Post-Test Calibration
1.6526	Final Specific Gravity Reading
1.6526	Final Specific Gravity Reading
-1.6524	Preliminary Specific Gravity Reading
0.0002	Maximum Correction

Figure 4. Sample Specific Gravity Calculation

Table 6 also contains density data derived from corrected specific gravity readings. Density was obtained by multiplying specific gravity, as measured at 15.56°C (60°F), by the density of water at the same temperature. For the example cited in Figure 4, the result was 1.6510 gm/cm<sup>3</sup>.

In order to determine "buoyancy effect," the curve for the density of each acid shown in Figure 3 was extrapolated, as required to 15.56°C (60°F). In only one case was extrapolation beyond 0.5°C required. The linearity of the curves justified such extrapolation. The results are shown in Table 6 in the column of "density values by pycnometer". The differences between the two columns of values for density are tabulated as "buoyancy effect." In all cases, positive errors were observed for hydrometer readings. Depending on the composition of the acid, the error could cause a significant difference in calculating rocket engine performance based on specific gravity data.

### 1.3 Vapor Pressure

A two-cube factorial experiment was designed to test for the variables controlling the equilibrium pressure of Modified HDA. For this type of test, eight solutions containing high and low concentrations of nitrogen dioxide, water and phosphorous pentafluoride were required.

In addition, the experiment was designed to determine the effect of temperature on equilibrium pressure. This was accomplished by use of an oven which was held at constant temperature until a stable reading of pressure was obtained. Additional readings were taken with the oven at higher temperatures.

Finally, the experiment was designed to separate the decomposition pressure component of equilibrium pressure from the vapor pressure component, at a fixed temperature. The former component arises from the generation of oxygen gas by decomposition of nitric acid, and the relatively low solubility of oxygen in Modified HDA. This objective was achieved by expanding the vapors above the sample into a second vessel. The pressure, due to decomposition, was evident as a reduction in equilibrium pressure. Further expansion into a third vessel confirmed the effect.

The eight stock solutions required for the two-cube factorial equilibrium pressure experiment were prepared and analyzed according to standard procedures. The composition of each stock solution is presented with PVT (Pressure Volume Temperature) data for that solution. The general form of the test matrix in terms of the concentration of the three components studied is shown in Table 7. The concentrations shown under comments are nominal, low and high values selected to represent the range in composition over which Modified HDA might be used in rocket engines. Further description of the nominal values is given on page 37, with reference to Table 12.

TABLE 7 VAPOR PRESSURE TEST MATRIX

Stock Solution	Relative Concentration			Comments
	NO <sub>2</sub>	H <sub>2</sub> O	PF <sub>5</sub>	
1	Low	Low	Low	41 wt % NO <sub>2</sub> , 0.4 wt % H <sub>2</sub> O, 0.5 wt % PF <sub>5</sub>
2	Low	Low	High	
3	Low	High	Low	
4	Low	High	High	
5	High	Low	Low	45 wt % NO <sub>2</sub> , 1.0 wt % H <sub>2</sub> O, 0.7 wt % PF <sub>5</sub>
6	High	Low	High	
7	High	High	Low	
8	High	High	High	

Figure 5 is a photograph of the assembly used for measuring the vapor pressure of each Modified HDA blend. The assembly consisted of three aluminum vessels (V) lined with Teflon, to present an inert environment to the acid. Each vessel was equipped with a thermistor (T), for measuring test temperature, and a pressure transducer (P). Test Vessel V<sub>1</sub> included a capped port (C<sub>1</sub>), for loading and unloading acid. A second, capped port (C<sub>2</sub>), on the line leading to the pressure transducer (P<sub>1</sub>), was included as a vent. A valve (X<sub>1</sub>), in the line between vessels V<sub>1</sub> and V<sub>2</sub>, allowed isolation of one vessel from the other. A similar valve (X<sub>2</sub>) allowed isolation of test vessel V<sub>2</sub> from test vessel V<sub>3</sub>. Valve X<sub>3</sub> on test vessel V<sub>3</sub> was used for pressurizing, evacuating or venting the assembly.

A separate vessel of known volume (V<sub>k</sub>) was attached to the vapor pressure assembly to effect calibration of the latter. Several arrangements were used, but all involved expanding nitrogen gas at constant temperature from a pressurized vessel(s) to an evacuated vessel(s), and measuring pressure before and after expansion. The known volume was a stainless steel tank with a valve on each side, and a vent cap opposite one of the valves. (See Figure 6.)

The known volume was cleaned and calibrated before use. The first calibration step consisted of evacuation. After the vessel reached room temperature (24.9°C (75.2°F)), the vessel was weighed. Next, the vessel was filled with distilled water at 24.9°C (75.2°F). Water remaining in the outlet of the fill valve was carefully removed. The full vessel was then reweighed. The volume of the vessel was calculated from the weight of water and its known density at the test temperature. The volume equaled 436.3 cm<sup>3</sup> (cubic centimeters).

Next, the vapor pressure assembly was tested for leaks. This was accomplished by attaching V<sub>k</sub> to V<sub>1</sub> by the fitting under C<sub>1</sub>. A nitrogen source was attached to X<sub>5</sub> on the known volume, and all valves but X<sub>3</sub> were opened. Nitrogen pressure was applied until a value of 90" Hg (inches of mercury) (3 atm(atmospheres)) was indicated from the output of the pressure transducers on each test vessel. The output was read from a multipoint recorder and electronic accessories provided for this

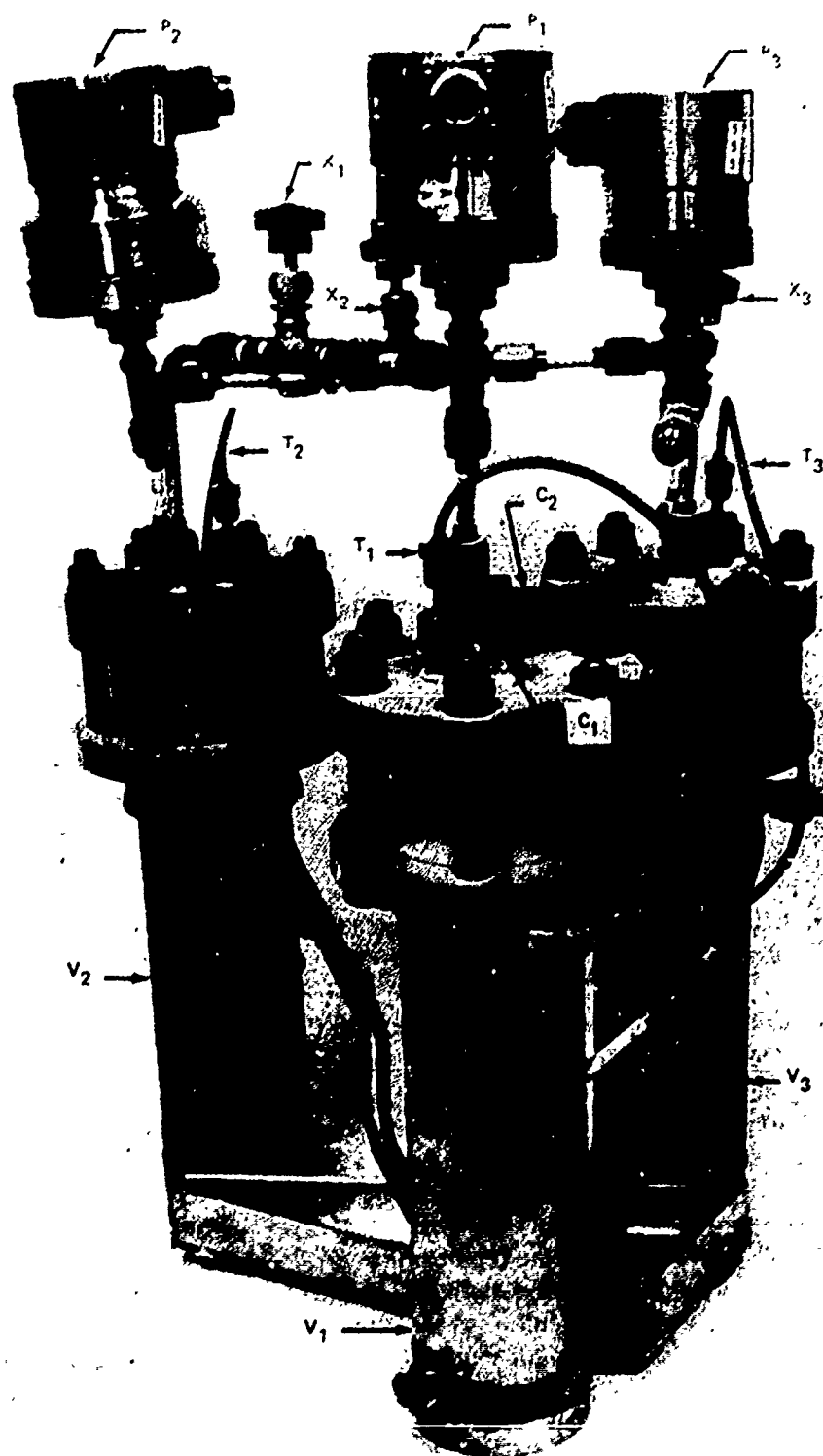


Figure 5. Vapor Pressure Test Vessels

purpose. The electronic accessories consisted of a DC power supply with a Zenner diode regulator to provide 9.5 volts to a series of Wheatstone bridges. There were four bridges for measuring temperature and three bridges for measuring pressure. One temperature bridge was connected to a decade resistor set at 984 ohms, equivalent to a temperature of 45°C (113°F). This bridge was used as a baseline for the other bridges, connected, one each to thermistors in  $V_1$ ,  $V_2$ , and  $V_3$ . Each bridge had a sensitivity of 21.1-48.9°C (70-120°F), and coarse and fine adjustments for precise balance at a given temperature. Balance was indicated on a scale on the recorder. The scale was calibrated from 21.1-48.9°C (70-120°F). Signals to the recorder were reinforced with a DC amplifier. Also recorded was the output from the decade resistor as a reference. In a similar manner, signals from the bridges, including the pressure transducers were recorded on a scale calibrated to 0-100" Hg (0-3.3 atm). Also recorded for the leak test was the temperature in each test vessel. Valves  $X_1$ ,  $X_2$ , and  $X_4$  were closed, and the assembly was allowed to stand at constant temperature. Temperature and pressure were monitored for 24 hours. With no leakage indicated for  $V_1$ ,  $V_2$  or  $V_3$ ,  $X_4$ , on the known volume was opened and  $V_k + V_1$  were observed for a change in pressure. No change was recorded. This certified the equipment as leak-free.

The leak test was repeated after moving  $V_k$  from  $V_1$  to  $V_3$ .  $C_1$  was replaced.  $V_k$  was attached to  $X_1$  as shown in Figure 6.

Calibration of the test vessels,  $V_1$ ,  $V_2$ ,  $V_3$ , continued as follows. With valves  $X_{1,4}$  open, nitrogen pressure was applied through  $X_5$  until a value of 90" Hg (3 atm) was indicated by the readout of pressure from the three transducers. In a similar manner, the temperature of the nitrogen in the test vessels was indicated by recorded data from the three thermistors in the test vessels. Valve  $X_1$  was closed and the nitrogen source was removed from  $X_5$ . The known volume was bled to one atmosphere and then evacuated. Valve  $X_5$  was closed, as were  $X_1$  and  $X_2$ . Valve  $X_3$  was opened, allowing gas to expand from  $V_3$  into the known volume. A slight drop in temperature occurred during expansion, but equilibrium conditions were soon re-established. The new pressure, corresponding to the volume of test vessel  $V_3$  plus the known volume, was noted. Valve  $X_2$  was opened next and the reduced pressure, corresponding to the total volume of the two test vessels and the known volume, was recorded. Finally,  $X_1$  was opened and the reduced pressure in the entire system was recorded from the output of the three transducers. The volume of each test vessel was calculated by use of the gas laws from the changes in pressure, following the steps described.

Using the same regulator setting which had provided the initial pressure for the initial calibration steps, a second set of data were obtained by a variation of the calibration procedure. The entire assembly was evacuated through valve  $X_5$ . Temperature and pressure data were recorded. Valves  $X_1$ ,  $X_4$  were closed. The nitrogen source was attached to  $X_5$  and the known volume was pressurized to 90" Hg (3 atm). The gas in  $V_k$  was expanded stepwise into the three test vessels. The pressure changes noted at each step were used for a second set of calculations of the test vessel volumes.

The known volume was then repositioned to test vessel  $V_1$ . Attachment was made to the fitting under  $C_1$ . After a satisfactory leak check, the known volume was evacuated, but the test vessels were pressurized to 90" Hg (3 atm).  $V_k$  was pressurized in steps by opening the valves between the test vessels. The volumes of the latter were calculated from the accompanying drops in pressure.

A final set of calibration steps involved stepwise expansion of nitrogen from  $V_k$  at 90" Hg (3 atm) into the evacuated test vessels, and calculation of the volume of the latter from measured changes in pressure at constant temperature. During the entire calibration procedure, temperature was maintained at  $24.2 \pm 0.3^\circ\text{C}$  ( $75.5 \pm 0.5^\circ\text{F}$ ).

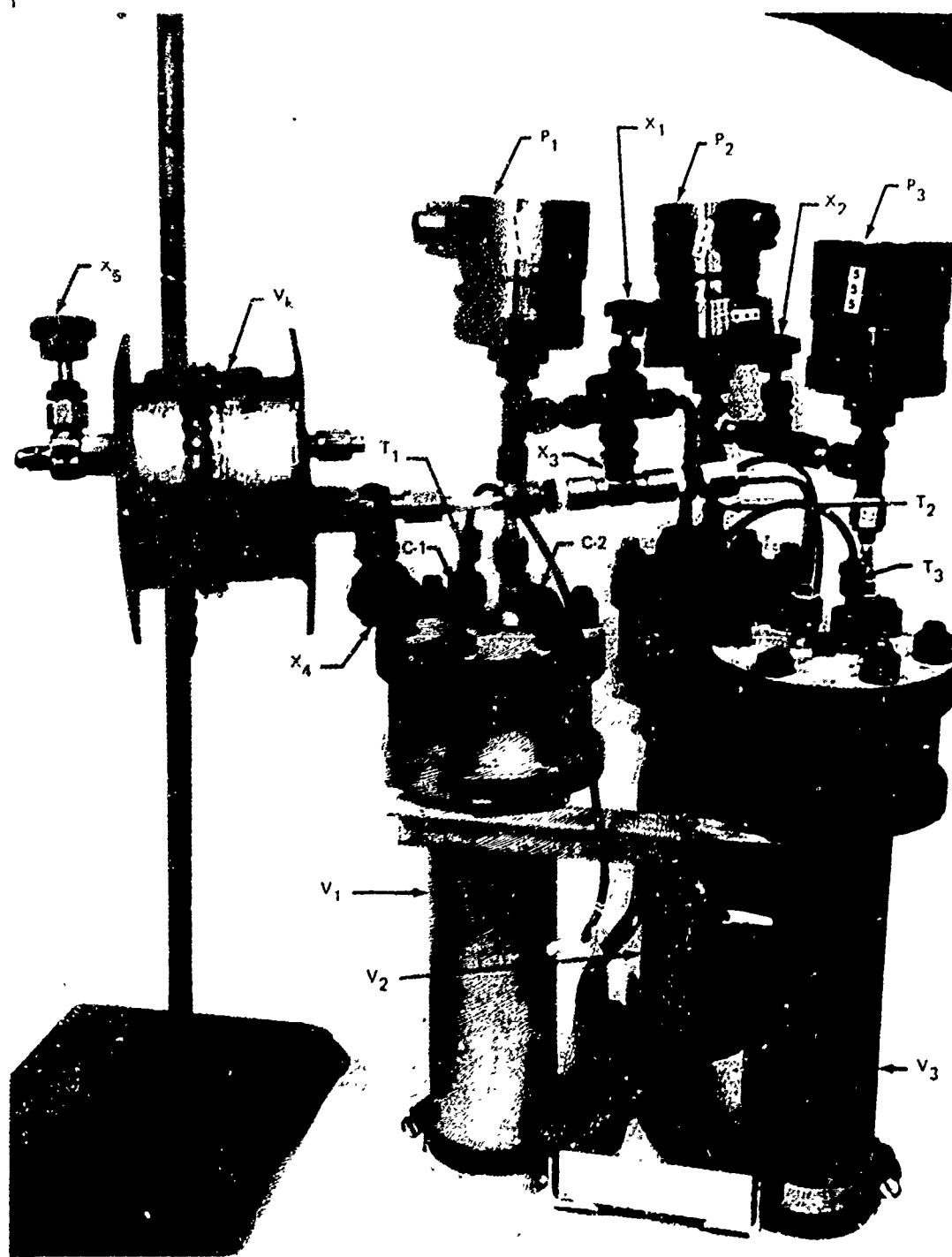


Figure 6. Calibration and Vapor Pressure Test Vessels

Close agreement was found for the volume of each test vessel calculated from data by the four variations cited in the calibration procedure. The average volume of each vessel is shown in Table 8.

TABLE 8. VAPOR PRESSURE CALIBRATION DATA

Vessel	Volume, cm <sup>3</sup>
V <sub>k</sub>	436.3
V <sub>1</sub>	237.2
V <sub>2</sub>	239.5
V <sub>3</sub>	236.2

These values were employed in subsequent vapor pressure measurements.

Vapor pressure measurements began with a set of steps carried out with the test assembly in a bench top hood. The test vessels were filled with nitrogen gas, then isolated from one another by their respective valves. A weighed amount of cold, stock solution was added to V<sub>1</sub> through a funnel temporarily attached to the fitting under C<sub>1</sub>. Some nitrogen was displaced through the temporarily exposed fitting under C<sub>2</sub>. Samples of acid were withdrawn from V<sub>1</sub>, inspected and analyzed for nitrogen dioxide and water contents. The caps were replaced, and the assembly was placed in an oven, in a walk-in hood, for the next set of steps. The oven had been calibrated previously to provide constant temperature over the range 25-47°C (77-117°F).

Thermistors and pressure transducers were connected to leads from a multipoint recorder and associated electronics on a cart next to the oven. A line was attached from valve X<sub>3</sub> to a liquid nitrogen trap, and this in turn was attached to a vacuum pump. See Figure 7 for the relative location of equipment used for the vapor pressure measurements. Note that the oven was installed in the walk-in hood as a safety precaution. The refrigerator for chilling and storing stock solutions was situated in another part of the hood.

With the oven at room temperature, any nitrogen remaining in V<sub>1</sub> was removed by evacuating V<sub>1</sub> and V<sub>3</sub>, then expanding the vapors in V<sub>1</sub> to the other vessels. The process was repeated three times. Valve X<sub>1</sub> was closed after each step to isolate test vessel V<sub>1</sub> and its contents for subsequent measurements at elevated temperatures.

The oven was set to a preselected temperature, T<sub>1</sub><sup>o</sup>, and readings were taken until thermal equilibrium was established in test vessel V<sub>1</sub>, as indicated by no further rise in pressure. The process was repeated at two higher temperatures, T<sub>2</sub><sup>o</sup> and T<sub>3</sub><sup>o</sup>.

After equilibrium was established at T<sub>3</sub><sup>o</sup>, vacuum was applied, as required, to reduce the pressure in test vessel V<sub>2</sub> to zero. The valve between test vessels V<sub>1</sub> and V<sub>2</sub> was opened, and pressure in V<sub>1</sub> and V<sub>2</sub> were monitored until thermal equilibrium was re-established. Temperature returned to T<sub>3</sub><sup>o</sup>, but the new pressure was less than the pressure measured before expansion. The process was repeated with test vessel V<sub>3</sub>. A further drop in pressure was observed, completing the test.

After the test, the assembly was moved to the other hood, for resampling and reloading. One set of samples was drawn from test vessel V<sub>1</sub>, after the acid had cooled to room temperature. Another set of samples was taken from a Kel-F bottle into which the rest of the acid was transferred from test vessel V<sub>1</sub> with nitrogen pressure. Physical appearance was noted and nitrogen dioxide and

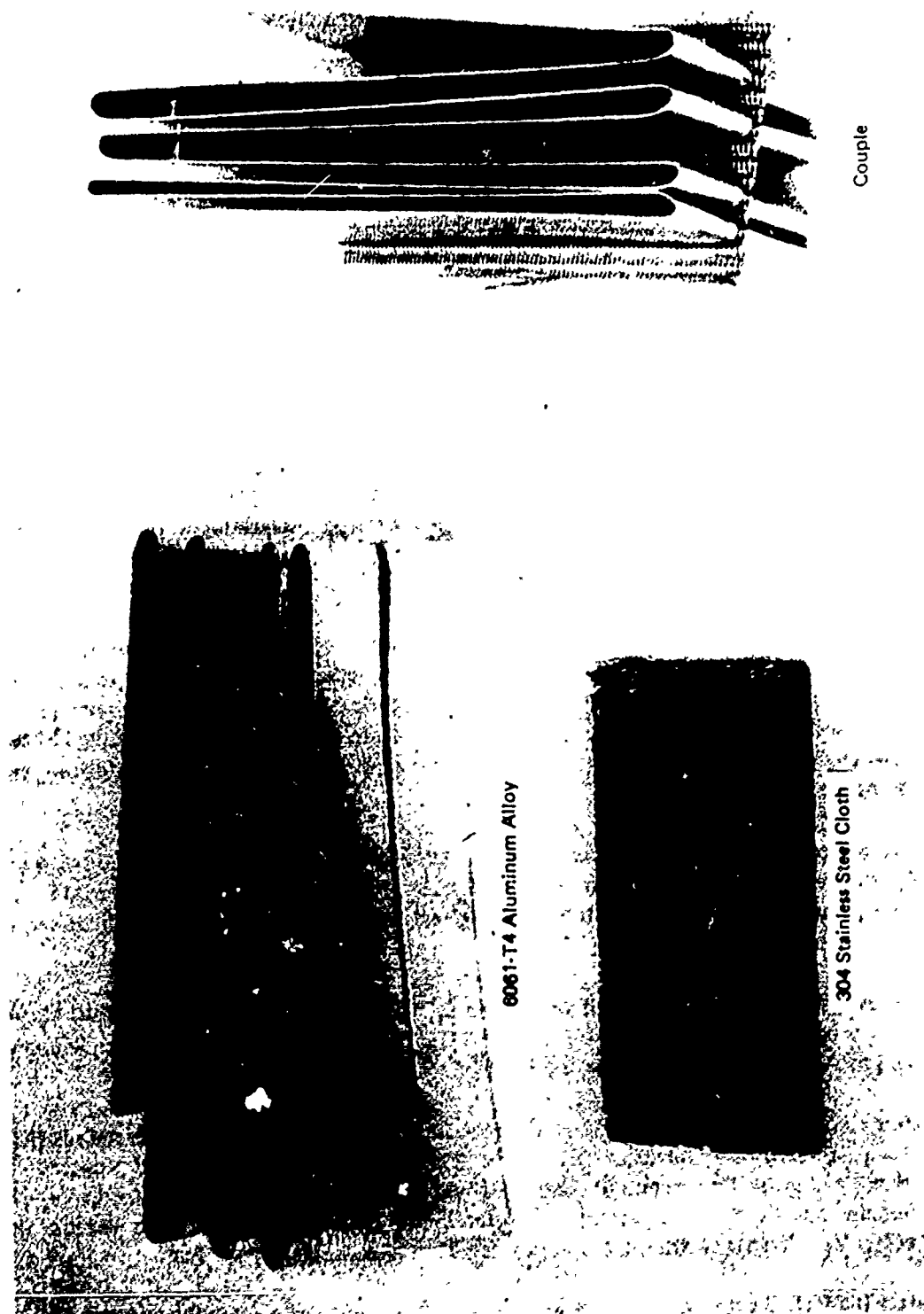


Figure 7. Vapor Pressure Test Equipment



water contents were measured, for both samples of acid. Phosphorous pentafluoride content was also determined for the sample in the bottle. This acid was refrigerated before analysis.

The entire procedure was repeated, beginning with addition of part of another stock solution to test vessel  $V_1$ .

The foregoing procedure was developed through five experiments designed to optimize test time and determine changes in composition to the acid being tested during evacuation, expansion, and resampling. Attainment of thermal equilibrium after test temperature had been changed was a slow process, with the net result that a single vapor pressure run took approximately three days. The only significant change noted in acid composition was a loss in nitrogen dioxide. The magnitude of this loss is indicated in Table 9, which contains the results of acid analyses made in support of each experiment, and PVT data collected in the course of the experiments.

In the first experiment, a portion of Modified HDA (stock solution P), with relatively low nitrogen dioxide and water contents and relatively high water content was subjected to test. This simulated the third solution in the test matrix. Acid analyses were made in support of the test, and are reported on the first page of Table 9. These analyses revealed that a higher concentration of nitrogen dioxide would be required initially to provide the level desired during test. The designation OK for physical appearance signifies that the acid contained a few particles of foreign material. The difference in weight between the amount of acid loaded and the residual acid represents the weight of acid lost through transfers, sampling, evacuation and purges. PVT data in Table 9 include pressure readings, accurate to  $\pm 0.5$  "Hg, and temperature readings, accurate to  $\pm 2.0^\circ\text{F}$ . Volume  $V_1$  represents the difference between the total volume of test vessel  $V_1$  and the volume of acid loaded into the vessel. The latter was derived from the weight of acid loaded, its temperature, and its density at that temperature. Density data were taken from Figure 3. Pressure readings below 2 "Hg for  $V_2$  and  $V_3$  reflect evacuation of these test vessels to minimize absorption of acid vapor from previous tests, and to provide a baseline before expansion of acid vapor into these vessels during the current test. Pressure readings for  $V_1$  at the three temperatures studied,  $T_1^\circ$ ,  $T_2^\circ$  and  $T_3^\circ$ , were converted to psia (pounds per square inch absolute), and plotted as a function of temperature. The pressure versus temperature plot is shown in Figure 8. Also shown are data subsequently obtained for stock solution 3, which contained an additional percent of nitrogen dioxide. The curves are labeled equilibrium pressure because they represent the sum of vapor pressure and decomposition pressure. This is evident from the pressure readings before and after expansions at  $T_3^\circ$ . Were vapor pressure alone involved, there would have been no drop in pressure with increasing vapor volume. Were decomposition pressure alone involved, lower pressures would have been observed than were actually measured. Calculation of decomposition pressure is covered in Part III, Technical Discussion. The magnitude of the effect of expansion is evident from the data in Table 10. Experimentally determined pressures have been converted from "Hg to atm.

The second experiment was performed to determine the loss in nitrogen dioxide associated with the evacuation and resampling steps of the standard procedure for measuring vapor pressure. A portion of Modified HDA (stock solution JB) with relatively low concentrations of nitrogen dioxide, water and phosphorous pentafluoride was selected for this experiment, because the nitrogen dioxide content was similar to that used for the first experiment. The experiment was terminated after  $T_2^\circ$  had been reached. No losses on expansion were introduced. Data from supporting chemical analyses and PVT data are shown in Table 9, page 2. Analysis of residual acid was waived and PVT data were not recorded after the initial evacuation step. Required analyses, however, were made and showed a loss in nitrogen dioxide content of 0.8 wt% during the evacuation and resampling steps. PVT data taken matched the pattern established during the first experiment.

TABLE 9. VAPOR PRESSURE EXPERIMENTS (1 of 5)

Supporting Acid Analyses												
Experiment No.	Sample	Phys. Appear.	wt %					ppm (w/w)				
			HNO <sub>3</sub>	NO <sub>2</sub>	H <sub>2</sub> O	PF <sub>5</sub>	M <sub>2</sub> O <sub>3</sub>	Fe	Cr	Ni	Al	Comments
1	Stock Solution - P	Clear	Bal.	42.1	1.0	0.5	<0.01	<1	<1	<1	<1	Low NO <sub>2</sub> - High H <sub>2</sub> O - Low PF <sub>5</sub> .
	Pvs Test	Clear	..	41.6	1.0	..	..	..	..	..	..	161 gm loaded at 40°F (4.4°C) ≡ 97.3 cm <sup>3</sup> .
	Purt Test	Clear	..	39.0	1.0	..	..	..	..	..	..	
	Residual Acid	OK	..	38.6	1.0	0.5	<0.01	2	<1	<1	<1	125 gm recovered
PVT Data												
Step	Test Vessel No. 1			Test Vessel No. 2			Test Vessel No. 3			Comments		
	P <sub>1</sub> "Hg	V <sub>1</sub> cm <sup>3</sup>	T <sub>1</sub> °F	P <sub>2</sub> "Hg	V <sub>2</sub> cm <sup>3</sup>	T <sub>2</sub> °F	P <sub>3</sub> "Hg	V <sub>3</sub> cm <sup>3</sup>	T <sub>3</sub> °F			
Start	38.0	137.3	79.5	30.0	239.5	80.4	30.0	236.2	80.6	Monday, 11:30 AM.		
First Evacuation	23.2	137.4	78.1	22.5	239.5	80.4	22.5	236.2	81.0	Monday, 1:20 PM.		
Second Evacuation	23.4	137.4	78.2	19.7	239.5	80.4	19.6	236.2	81.0	Monday, 1:45 PM.		
Third Evacuation	20.9	137.5	75.5	19.3	239.5	79.3	19.3	236.2	80.8	Monday, 3:15 PM.		
Temperature, T <sub>1</sub> °	24.0	137.1	79.7	<1.0	239.5	80.0	<1.0	236.2	80.6	Monday, 9:30 PM.		
Temperature, T <sub>2</sub> °	34.2	136.4	93.1	1.0	239.5	93.5	1.0	236.2	93.4	Tuesday, 10:30 AM.		
Temperature, T <sub>3</sub> °	46.2	135.6	104.0	<0.1	239.5	105.2	<0.1	236.2	104.6	Tuesday, 12:00 AM.		
First Expansion	43.7	135.6	104.1	43.5	239.5	104.8	<0.1	236.2	104.4	Tuesday, 1:45 PM.		
Second Expansion	42.0	135.6	103.4	41.9	239.5	104.3	41.9	236.2	103.8	Wednesday 8:30 AM.		
Stop	20.0	137.5	75.5	2.0	239.5	75.0	1.3	236.2	75.7			

TABLE 9 VAPOR PRESSURE EXPERIMENTS (CONT.)

Supporting Acid Analyses													
Experiment No.	Sample	Phys. Appearance	wt %					ppm (w/w)					Comments
			HNO <sub>3</sub>	NO <sub>2</sub>	H <sub>2</sub> O	PF <sub>5</sub>	M <sub>2</sub> O <sub>3</sub>	Fe	Cr	Ni	Al		
2	Stock Solution -JB	Clear	Bal.	41.2	0.4	0.6	0.02	22	6	5	4	LOW NO <sub>2</sub> - Low H <sub>2</sub> O - Low PF <sub>5</sub> . 168 gm loaded at 44.5 (6.7°C) ≡ 101.5 cm <sup>3</sup>  149 gm recovered	
	Pri Test	Clear		40.5	0.4								
	Post Test	Clear		40.1	0.4								
	Residual Acid												
PVT Data													
Step	Test Vessel No. 1			Test Vessel No. 2			Test Vessel No. 3			Comments			
	P <sub>1</sub> "Hg	V <sub>1</sub> cm <sup>3</sup>	T <sub>1</sub> °F	P <sub>2</sub> "Hg	V <sub>2</sub> cm <sup>3</sup>	T <sub>2</sub> °F	P <sub>3</sub> "Hg	V <sub>3</sub> cm <sup>3</sup>	T <sub>3</sub> °F				
Start	32.7	133.7	73.4	0.2	239.5	74.2	< 0.1	236.2	74.9	Thursday 10:00 AM.			
First Evacuation										Not Recorded.			
Second Evacuation	17.2	133.8	71.4	15.0	239.5	72.4	14.8	236.2	75.0				
Third Evacuation	16.8	133.9	70.4	14.8	239.5	73.7	14.6	236.2	74.8	Thursday, 10:30 AM.			
Temperature, T <sub>1</sub> °	23.7	133.1	81.1	0.6	239.5	81.8	0.2	236.2	82.1	Thursday, 2:00 PM.			
Temperature, T <sub>2</sub> °										Waived.			
Temperature, T <sub>3</sub> °													
First Expansion													
Second Expansion													
Stop	23.8	133.1	81.3	0.5	239.5	82.0	0.2	236.2	82.2	Thursday, 2:30 PM.			

TABLE 9. VAPOR PRESSURE EXPERIMENTS (3 of 5)

Supporting Acid Analyses												
Experiment No.	Sample	Phys. Appar.	wt %					ppm (w/w)				
			HNO <sub>3</sub>	NO <sub>2</sub>	H <sub>2</sub> O	PF <sub>5</sub>	M <sub>2</sub> O <sub>3</sub>	Fe	Cr	Ni	Al	Comments
3	Stock Solution - JB	Clear	Bal.	41.2	0.4	0.6	0.02	22	6	5	4	Low NO <sub>2</sub> - Low H <sub>2</sub> O - Low PF <sub>5</sub> .
	Pie Test	Clear	..	41.2	0.3	..	..	..	..	..	..	170.5 gm loaded at 30°F (-0.6°C) ≡ 102.1 cm <sup>3</sup> .
	Pist Test	Clear	..	41.0	0.3	..	..	..	..	..	..	..
	Residual Acid	..	..	..	..	..	..	..	..	..	..	150 gm recovered.
PVT Data												
Step	Test Vessel No. 1			Test Vessel No. 2			Test Vessel No. 3			Comments		
	P <sub>1</sub> "Hg	V <sub>1</sub> cm <sup>3</sup>	T <sub>1</sub> °F	P <sub>2</sub> "Hg	V <sub>2</sub> cm <sup>3</sup>	T <sub>2</sub> °F	P <sub>3</sub> "Hg	V <sub>3</sub> cm <sup>3</sup>	T <sub>3</sub> °F			
Start	34.0	132.1	73.3	0.2	239.5	76.3	<0.1	236.2	76.7	Friday, 11:00 AM.		
First Evacuation	..	..	..	..	..	..	..	..	..	Waived.		
Second Evacuation	..	..	..	..	..	..	..	..	..			
Third Evacuation	..	..	..	..	..	..	..	..	..			
Temperature, T <sub>1</sub> °	40.2	131.5	81.7	0.3	239.5	81.9	<0.1	236.2	82.3	Friday, 2:30 PM.		
Temperature, T <sub>2</sub> °	..	..	..	..	..	..	..	..	..			
Temperature, T <sub>3</sub> °	..	..	..	..	..	..	..	..	..			
First Expansion	..	..	..	..	..	..	..	..	..			
Second Expansion	..	..	..	..	..	..	..	..	..			
Stop	39.9	131.6	80.8	..	..	..	..	..	..	Friday, 3:30 PM.		

TABLE 9 VAPOR PRESSURE EXPERIMENTS (4 of 5)

Supporting Acid Analyses													
Experiment No.	Sample	Phys. Appear	wt %					ppm (w/w)					Comments
			HNO <sub>3</sub>	NO <sub>2</sub>	H <sub>2</sub> O	PF <sub>5</sub>	M <sub>2</sub> O <sub>3</sub>	Fe	Cr	Ni	Al		
4	Stock Solution JB	Clear	Bar	41.2	0.4	0.6	0.02	22	6	5	4	Low NO <sub>2</sub> , Low H <sub>2</sub> O Low PF <sub>5</sub>	140 gm recovered
	Pix Test	Clear		40.9	0.4							170 gm loaded at 32 °C (0 °C) ≡ 101.8 cm <sup>3</sup>	
	Pix Test	Clear		40.2	0.4								
	Residual Acid												
PVT Data													
State	Test Vessel No. 1			Test Vessel No. 2			Test Vessel No. 3			Comments			
	P <sub>1</sub> (Hg)	V <sub>1</sub> cm <sup>3</sup>	T <sub>1</sub> °F	P <sub>2</sub> "Hg	V <sub>2</sub> cm <sup>3</sup>	T <sub>2</sub> °F	P <sub>3</sub> "Hg	V <sub>3</sub> cm <sup>3</sup>	T <sub>3</sub> °F				
Start	32.8	134.6	71.0	0.2	239.5	74.2	<0.1	236.2	76.0	Tuesday 10 00 AM			
First Evacuation										Waived.			
Second Evacuation													
Third Evacuation													
Temperature, T <sub>1</sub> °													
Temperature, T <sub>2</sub> °													
Temperature, T <sub>3</sub> °	60.8	132.3	103.8	<0.1	239.5	104.7	<0.1	236.2	104.1	Tuesday, 4:45 PM.			
First Expansion	46.7	132.1	106.2	46.4	239.5	107.1	<0.1	236.2	106.3	Tuesday, 8:15 PM.			
Second Expansion	44.8	132.1	106.1	44.6	239.5	106.8	44.8	236.2	106.1	Tuesday, 10:30 PM.			
Stop	21.1	134.1	77.9	4.4	239.5	77.2	4.2	236.2	77.9	Wednesday, 8:25 AM.			

TABLE 9. VAPOR PRESSURE EXPERIMENTS (5 of 5)

Supporting Acid Analyses											
Experiment No.	Sample	Phys. Appear.	wt %					ppm (w/w)			
			HNO <sub>3</sub>	NO <sub>2</sub>	H <sub>2</sub> O	PF <sub>5</sub>	M <sub>2</sub> O <sub>3</sub>	Fe	Cr	Ni	Al
5	Stock Solution - 5	Clear	Bal.	47.2	0.4	0.56	<0.01	1	<1	<1	<1
	Pre Test	Clear	--	46.9	0.4	--	--	--	--	--	--
	Post Test	Clear	--	44.6	0.5	--	--	--	--	--	--
	Revised Acid	Ok	--	44.8	0.4	0.55	--	--	--	--	--
High NO <sub>2</sub> - Low H <sub>2</sub> O - Low PF <sub>5</sub> . 170.2 gm loaded at 35° F (1.7°C) ≡ 102.4 cm <sup>3</sup> . 140.7 gm recovered.											
PVT Data											
Strip	Test Vessel No. 1			Test Vessel No. 2			Test Vessel No. 3			Comments	
	P <sub>1</sub> "Hg	V <sub>1</sub> cm <sup>3</sup>	T <sub>1</sub> °F	P <sub>2</sub> "Hg	V <sub>2</sub> cm <sup>3</sup>	T <sub>2</sub> °F	P <sub>3</sub> "Hg	V <sub>3</sub> cm <sup>3</sup>	T <sub>3</sub> °F		
Start	37.2	132.3	71.4	0.3	239.5	79.0	<0.1	236.2	80.0	Thursday, 2:15 P.M.	
First Evacuation	25.7	132.0	75.5	23.0	239.5	79.4	23.0	236.2	91.1	Thursday, 2:23 P.M.	
Second Evacuation	24.2	132.1	73.9	22.8	239.5	79.3	22.8	236.2	80.5	Thursday, 2:32 P.M.	
Third Evacuation	23.2	132.2	73.6	21.9	239.5	79.2	21.8	236.2	80.4	Thursday, 4:50 P.M.	
Temperature, T <sub>1</sub> °	29.0	131.6	80.8	2.1	239.5	80.6	2.1	236.2	81.1		
Temperature, T <sub>2</sub> °	--	--	--	--	--	--	--	--	--		
Temperature, T <sub>3</sub> °	--	--	--	--	--	--	--	--	--		
First Expansion	--	--	--	--	--	--	--	--	--		
Second Expansion	--	--	--	--	--	--	--	--	--		
Stop	24.3	132.1	74.5	4.0	239.5	73.8	3.3	236.2	74.6	Friday, 8:40 A.M.	

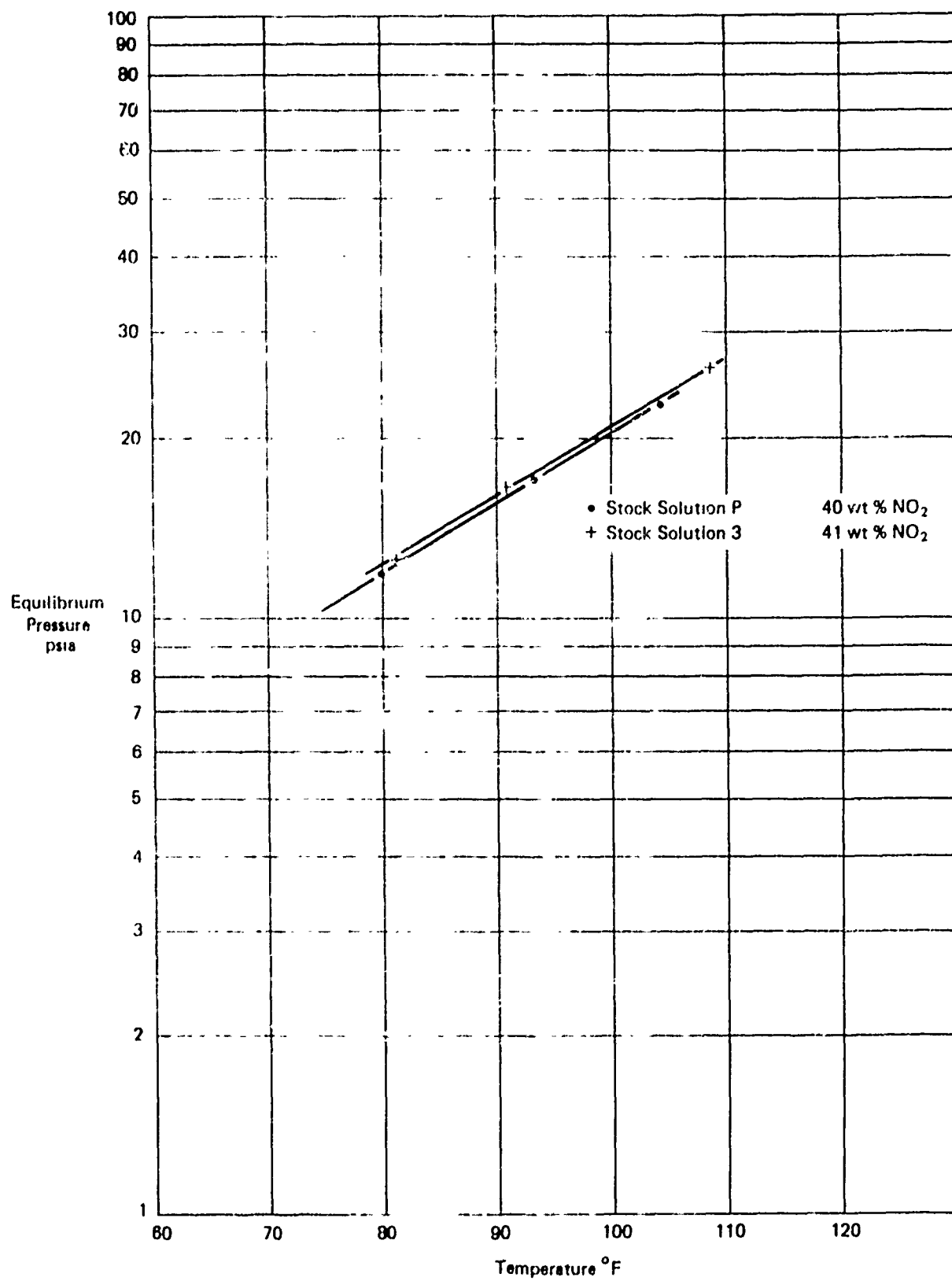


Figure 8. Vapor Pressure Experiment

TABLE 10. DECOMPOSITION PRESSURE - EXPERIMENT 1

Step	Pressure, atm
Temperature, $T_3^{\circ}$	1.54
After First Expansion	1.46
After Second Expansion	1.40

The third experiment was conducted with the object of determining how much of the 0.8 wt % loss of nitrogen dioxide found through the previous experiment was attributable to evacuation of the acid at the start of the standard procedure for measuring vapor pressure. This was accomplished by loading another portion of stock solution JB into test vessel  $V_1$  and raising temperature to  $T_1^{\circ}$ , without performing the standard evacuation steps. Data collected in support of this experiment are given in Table 9, page 3. The slight differences in water contents measured during the test are another reflection of the accuracy of the method. The differences in nitrogen dioxide content also fall within the limits of the method. Replicate analyses, however, established the likely loss of nitrogen dioxide during resampling as 0.2 wt %. Therefore, of the total loss of 0.8 wt % nitrogen dioxide during evacuation and resampling, 0.6 wt % was due to the evacuation steps. Analysis of residual acid was waived. The PVT data showed higher pressures in this experiment than in the one before due to the pressure, in the present case, of nitrogen as well as acid vapors in the ullage space of test vessel  $V_1$ .

Loss of nitrogen dioxide due to expansion of acid vapors was determined in a fourth experiment, with another portion of stock solution JB. The experimental objective was achieved by eliminating evacuation steps and measurements at temperatures  $T_1^{\circ}$  and  $T_2^{\circ}$ . In other respects, the standard vapor pressure measurement procedure was followed. The chemical analyses and PVT data collected during this experiment are shown in Table 9, page 4. Chemical analyses showed a net decrease of 0.5 wt % nitrogen dioxide, during the expansion steps. PVT data at temperature  $T_3^{\circ}$  again indicated the presence of nitrogen in test vessel  $V_1$ , because of deliberate elimination of the standard evacuation steps. Test vessels  $V_2$  and  $V_3$  were evacuated after the second expansion step had been completed. The small pressures noted for these vessels the following day represent outgassing of the Teflon liners in the vessels. The liners had absorbed some acid vapors while thermal equilibrium was being established.

The fifth experiment was similar to the second one except that Modified HDA with a relatively high nitrogen dioxide content (stock solution 5) was used. This was done to determine the effect of an initial, high nitrogen dioxide content on loss during the evacuation steps of the standard vapor pressure measurement procedure. Chemical analyses and PVT data collected are given in Table 9, page 5. Analytical results revealed a much larger loss (2.3 wt %) of nitrogen dioxide due to the evacuation and resampling steps. This was confirmed by analysis of the residual acid taken from test vessel  $V_1$  after test and chilled before analysis. Analysis of the same sample showed virtually no change in the concentrations of water or phosphorous pentafluoride. The point is emphasized by statement of results in hundredths rather than rounding off to tenths, as is normally done in keeping with the accuracy of the method. The PVT data prove further that an increase in nitrogen dioxide content will cause an increase in pressure at a given temperature.

The results of the five experiments in terms of nitrogen dioxide losses at critical steps in the experimental procedure are summarized in Table 11.

The eight stock solutions required for vapor pressure measurements were prepared on the basis of the first experiment to contain initially an additional percent of nitrogen dioxide above that in the originally planned test matrix. The results of the other experiments disclosed that losses incurred were higher than provided for, with the net effect that the nitrogen dioxide levels tested were



TABLE 11. NITROGEN DIOXIDE LOSSES

Step	wt %	Comment
Evacuation	2.1	HDA with High NO <sub>2</sub> Content.
Evacuation	0.6	HDA with Low NO <sub>2</sub> Content.
Expansion	0.6	
Resampling	0.2	

instead one percent less than originally planned. Since the difference in levels was maintained at 4 wt% nitrogen dioxide, these somewhat lower levels of nitrogen dioxide did not affect the design of the two-cube factorial evaluation of variables. The test matrix in terms of the stock solutions as tested is as shown in Table 12. As stated on page 23, and indicated in the caption below, nominal concentrations for NO<sub>2</sub>, H<sub>2</sub>O and PF<sub>5</sub> are tabulated. These values were rounded off to the number of significant figures consistent with the accuracy of the analyses, the results of preliminary vapor pressure experiments, and the results of the vapor pressure runs.

TABLE 12. NOMINAL CONCENTRATIONS OF VAPOR PRESSURE STOCK SOLUTIONS

Stock Solution	wt %			Comments
	NO <sub>2</sub>	H <sub>2</sub> O	PF <sub>5</sub>	
1	41	0.4	0.5	Low - Low - Low
2	41	0.4	0.7	Low - Low - High
3	41	1.0	0.5	Low - High - Low
4	42	1.0	0.7	Low - High - High
5	45	0.4	0.5	High - Low - Low
6	45	0.4	0.7	High - Low - High
7	45	1.0	0.5	High - High - Low
8	45	1.0	0.7	High - High - High

The intermediate nitrogen dioxide content of stock solution 4 was unintended, but the results from the experiment with this solution strengthened the overall conclusions drawn.

Each stock solution was subjected to the standard procedure for measuring vapor pressure. Data from supporting chemical analyses and PVT data are given in Table 13. The arrangement of the table is the same as the arrangement used to present data from the vapor pressure experiments. The pages of Table 13 are arranged by stock solution number rather than by the order in which the vapor pressure runs were made. The run numbers are, however, included in the table for reference.

With reference to supporting chemical analyses, it will be noted that the NO<sub>2</sub> (nitrogen dioxide) contents reported are as measured by a procedure with an accuracy of  $\pm 0.5$  wt % NO<sub>2</sub>. The decreases in nitrogen dioxide content at check points during the test are consistent with the results of the experiments previously described. Higher values were generally obtained for nitrogen dioxide content from the larger, chilled sample of residual acid emptied from the test vessel, than for the sample drawn directly from the relatively warm vessel post test. During the courses of the runs, the calibration curve for water content was confirmed. Values are reported to the nearest tenth percent,

TABLE 13. VAPOR PRESSURE RUNS (1 of 8)

Supporting Acid Analyses											
Run No.	Sample	Phys. Appear.	wt %					ppm (w/w)			
			HNO <sub>3</sub>	NO <sub>2</sub>	H <sub>2</sub> O	PF <sub>5</sub>	M <sub>2</sub> O <sub>3</sub>	Fe	Cr	Ni	Al
4	Stock Solution - 1	Clear	Bal.	43.0	0.4	0.55	<0.01	1	<1	<1	<1
	First Test	Clear	..	42.8	0.4	..	..	..	..	..	..
	First Test	Clear	..	40.6	0.4	..	..	..	..	..	..
	Residual Acid	Clear	Bal.	41.3	0.4	0.56	<0.01	3	<1	<1	<1
Comments											
Low NO <sub>2</sub> - Low H <sub>2</sub> O - Low PF <sub>5</sub> . 167.0 gm loaded at 30.0°F (-1.1°C) ≡ 100.2 cm <sup>3</sup> . 135.0 gm recovered.											
PVT Data											
Step	Test Vessel No. 1			Test Vessel No. 2			Test Vessel No. 3			Comments	
	P <sub>1</sub> "Hg	V <sub>1</sub> cm <sup>3</sup>	T <sub>1</sub> °F	P <sub>2</sub> "Hg	V <sub>2</sub> cm <sup>3</sup>	T <sub>2</sub> °F	P <sub>3</sub> "Hg	V <sub>3</sub> cm <sup>3</sup>	T <sub>3</sub> °F		
Start	33.9	134.1	72.6	< 0.1	239.5	76.1	< 0.1	236.2	75.2	Tuesday, 11:30 AM.	
First Evacuation	19.9	134.1	72.2	19.0	239.5	76.3	18.9	236.2	75.6	Tuesday, 11:45 AM.	
Second Evacuation	18.8	134.2	71.6	17.8	239.5	76.4	17.7	236.2	75.5		
Third Evacuation	18.0	134.2	70.7	17.2	239.5	76.4	17.1	236.2	75.4	Tuesday, 12:00 AM.	
Temperature, T <sub>1</sub>	24.7	133.6	80.1	1.6	239.5	80.9	1.4	236.2	80.6	Tuesday, 3:00 PM.	
Temperature, T <sub>2</sub>	37.1	132.5	95.0	2.8	239.5	95.4	2.4	236.2	96.4	Tuesday, 9:30 PM.	
Temperature, T <sub>3</sub>	52.2	131.5	108.7	4.9	239.5	108.3	4.0	236.2	109.7	Wednesday, 8:45 AM.	
First Expansion	48.2	131.6	108.0	49.1	239.5	107.7	0.5	236.2	108.5	Wednesday, 2:30 PM.	
Second Expansion	48.0	131.5	108.1	48.0	239.5	107.8	48.0	236.2	108.9	Wednesday, 4:30 PM.	
Stop	20.0	133.9	75.6	5.3	239.5	75.7	5.0	236.2	75.0	Thursday, 8:20 AM.	

TABLE 13 VAPOR PRESSURE RUNS (2 of 8)

Supporting Acid Analyses												
Run No.	Sample	Phys. Appearance	wt %					ppm (w/w)				
			HNO <sub>3</sub>	NO <sub>2</sub>	H <sub>2</sub> O	PF <sub>5</sub>	M <sub>2</sub> O <sub>3</sub>	Fe	Cr	Ni	Al	Comments
7	Stock Solution - 2	Clear	Bal.	43.3	0.4	0.72	<0.01	1	<1	<1	<1	Low NO <sub>2</sub> ; Low H <sub>2</sub> C - High PF <sub>5</sub> .
	Pre Test	Clear		43.3	0.4							170.0 gm loaded at 39.0°F (3.9°C) ≡ 102.3 cm <sup>3</sup>
	Post Test	Clear		41.0	0.4							
	Residual Acid	Clear		41.2	0.4	0.74		2	<1	<1		141.0 gm recovered
PVT Data												
Step	Test Vessel No. 1				Test Vessel No. 2				Test Vessel No. 3			
	P <sub>1</sub> "Hg	V <sub>1</sub> cm <sup>3</sup>	T <sub>1</sub> °F	P <sub>2</sub> "Hg	V <sub>2</sub> cm <sup>3</sup>	T <sub>2</sub> °F	P <sub>3</sub> "Hg	V <sub>3</sub> cm <sup>3</sup>	T <sub>3</sub> °F	P <sub>4</sub> "Hg	V <sub>4</sub> cm <sup>3</sup>	Comments
Start	33.1	132.6	73.0	0.3	239.5	77.8	<0.1	236.2	77.5			Wednesday, 1:30 PM.
First Evacuation	20.4	132.6	72.8	19.2	239.5	78.3	19.1	236.2	78.8			
Second Evacuation	20.0	132.6	72.5	18.2	239.5	78.2	18.1	236.2	78.8			
Third Evacuation	19.1	132.6	71.9	18.0	239.5	76.1	17.8	236.2	77.5			Wednesday, 1:40 PM.
Temperature, T <sub>1</sub> °	25.2	132.0	81.9	1.6	239.5	81.0	1.4	236.2	81.6			Wednesday, 6:00 PM.
Temperature, T <sub>2</sub> °	32.6	131.0	95.3	4.9	239.5	95.2	3.9	236.2	94.9			Thursday, 9:45 AM.
Temperature, T <sub>3</sub> °	55.9	129.8	111.6	6.9	239.5	112.2	5.2	236.2	110.7			Thursday, 7:45 PM.
First Expansion	53.0	129.8	111.2	52.9	239.5	111.5	1.8	236.2	110.3			Friday, 8:30 AM.
Second Expansion	52.0	129.8	111.0	51.9	239.5	111.6	52.0	236.2	110.2			Friday, 11:00 AM.
Stop	24.0	132.0	81.2	0.7	239.5	80.0	0.2	236.2	80.0			Friday, 1:45 PM.

TABLE 13. VAPOK PRESSURE RUNS (3 of 8)

Supporting Acid Analyses											
Run No.	Sample	Phys. Appear.	wt %					ppm (w/w)			
			HNO <sub>3</sub>	NO <sub>2</sub>	H <sub>2</sub> O	PF <sub>5</sub>	M <sub>2</sub> O <sub>3</sub>	Fe	Cr	Ni	Al
1	Stock Solution - 3	Clear	Bel.	42.7	1.0	0.55	<0.01	1	<1	<1	<1
	Pre Test	Clear	..	42.7	1.0	..	..	..	..	..	..
	Post Test	Clear	..	40.0	1.0	..	..	..	..	..	..
	Residual Acid	Clear	Bel.	40.3	1.0	0.55	<0.01	3	<1	<1	<1
PVT Data											
Step	Test Vessel No. 1			Test Vessel No. 2			Test Vessel No. 3			Comments	
	P <sub>1</sub> "Hg	V <sub>1</sub> cm <sup>3</sup>	T <sub>1</sub> °F	P <sub>2</sub> "Hg	V <sub>2</sub> cm <sup>3</sup>	T <sub>2</sub> °F	P <sub>3</sub> "Hg	V <sub>3</sub> cm <sup>3</sup>	T <sub>3</sub> °F		
Start	33.0	133.5	71.9	0.2	239.5	76.0	0.1	236.2	76.7	Wednesday, 9:45 AM.	
First Evacuation	20.4	133.5	71.7	19.7	239.5	76.3	19.6	236.2	76.2		
Second Evacuation	19.7	133.6	70.5	18.6	239.5	74.4	18.5	236.2	76.2		
Third Evacuation	18.8	133.6	70.0	17.9	239.5	74.2	17.8	236.2	76.2	Wednesday, 10:00 AM.	
Temperature, T <sub>1</sub> °	25.3	132.8	81.1	1.0	239.5	80.7	0.3	236.2	81.1	Wednesday, 12:00 AM.	
Temperature, T <sub>2</sub> °	33.8	132.1	90.7	1.1	239.5	91.7	0.5	236.2	91.6	Wednesday, 2:45 PM.	
Temperature, T <sub>3</sub> °	53.0	130.8	108.5	2.2	239.5	109.2	1.4	236.2	108.3	Wednesday, 9:45 PM.	
First Expansion:	52.7	130.7	109.9	52.6	239.5	110.2	0.2	236.2	109.4	Thursday, 8:15 AM.	
Second Expansion	50.0	130.8	108.4	49.9	239.5	109.5	49.9	236.2	108.7	Thursday, 10:45 AM.	
Stop	26.0	132.7	83.0	2.6	239.5	81.5	2.4	236.2	81.5	Thursday, 1:35 PM.	

TABLE 13. VAPOR PRESSURE RUNS (4 of 8)

Supporting Acid Analyses												
Run No.	Sample	Phys. Appearance	wt %					ppm (w/w)				
			HNO <sub>3</sub>	NO <sub>2</sub>	H <sub>2</sub> O	PF <sub>5</sub>	M <sub>2</sub> O <sub>3</sub>	Fe	Cr	Ni	A.	Comments
3	Stock Solution - 4	Clear	Bal.	43.6	1.0	0.72	<0.01	1	<1	<1	<1	Low NO <sub>2</sub> - High H <sub>2</sub> O - High PF <sub>5</sub> .
	Pri. Test	Clear		33.6	1.0							168.5 gm loaded at 36.0°F (2.2°C) ≡ 101.5 cm <sup>3</sup> .
	Post Test	Clear		41.3	1.0							
	Residual Acid	Clear	Bal.	40.6	1.0	0.74	<0.01	4	<1	<1	<1	135.8 gm recovered
PVT Data												
Step	Test Vessel No. 1				Test Vessel No. 2				Test Vessel No. 3			
	P <sub>1</sub> "Hg	V <sub>1</sub> cm <sup>3</sup>	T <sub>1</sub> °F	P <sub>2</sub> "Hg	V <sub>2</sub> cm <sup>3</sup>	T <sub>2</sub> °F	P <sub>3</sub> "Hg	V <sub>3</sub> cm <sup>3</sup>	T <sub>3</sub> °F	Comments		
Start	33.9	133.3	71.8	0.3	239.5	75.8	0.1	236.2	76.9	Wednesday, 10:30 AM.		
First Evacuation	21.7	133.3	71.5	20.0	239.5	76.2	19.9	236.2	77.2			
Second Evacuation	20.8	133.4	70.3	19.4	239.5	76.2	19.3	236.2	77.4			
Third Evacuation	20.0	133.4	70.3	18.8	239.5	76.2	18.7	236.2	77.3	Wednesday, 10:45 AM.		
Temperature, T <sub>1</sub> °	26.2	132.7	79.6	1.8	239.5	79.5	1.6	236.2	80.1	Wednesday, 2:00 PM.		
Temperature, T <sub>2</sub> °	42.8	131.4	97.2	3.8	239.5	98.6	3.2	236.2	98.3	Wednesday, 9:15 PM.		
Temperature, T <sub>3</sub> °	59.2	130.4	111.0	6.6	239.5	111.9	4.8	236.2	110.9	Thursday, 9:00 AM.		
First Expansion	55.3	130.6	109.4	55.2	239.5	110.6	0.2	236.2	110.5	Thursday, 1:15 PM.		
Second Expansion	54.1	130.6	109.2	53.9	239.5	110.7	54.0	236.2	109.9	Thursday, 4:00 PM.		
Stop	22.6	132.9	76.4	10.3	239.5	75.9	10.3	236.2	76.7	Friday, 8:20 AM.		

TABLE 13. VAPOR PRESSURE RUNS (5 of 8)

Supporting Acid Analyses												
Run No.	Sample	Phys. Appear.	wt %					ppm (w/w)				
			HNO <sub>3</sub>	NO <sub>2</sub>	H <sub>2</sub> O	PF <sub>5</sub>	M <sub>2</sub> O <sub>3</sub>	Fe	Cr	Ni	Al	Comments
5	Stock Solution - 5	Clear	Bal.	47.2	0.4	0.56	<0.01	1	<1	<1	<1	High NO <sub>2</sub> - Low H <sub>2</sub> O - Low PF <sub>5</sub> .
	Pre Test	Clear	..	47.0	0.4	..	..	..	..	..	..	169.0 gm loaded at 37.0°F (2.8°C) ≡ 101.8 cm <sup>3</sup> .
	Post Test	Clear	..	44.2	0.4	..	..	..	..	..	..	
	Residual Acid	Clear	..	43.9	0.4	0.57	..	2	..	..	..	137.5 gm recovered.
PVT Data												
Step	Test Vessel No. 1				Test Vessel No. 2				Test Vessel No. 3			
	P <sub>1</sub> "Hg	V <sub>1</sub> cm <sup>3</sup>	T <sub>1</sub> °F	P <sub>2</sub> "Hg	V <sub>2</sub> cm <sup>3</sup>	T <sub>2</sub> °F	P <sub>3</sub> "Hg	V <sub>3</sub> cm <sup>3</sup>	T <sub>3</sub> °F	Comments		
Start	35.0	132.9	73.2	< 1.0	239.5	76.4	< 1.0	236.2	77.1	Wednesday, 10:45 AM.		
First Evacuation	23.8	133.0	72.3	22.2	239.5	76.8	22.2	236.2	77.5			
Second Evacuation	22.8	133.0	71.6	21.1	239.5	76.5	21.1	236.2	77.5			
Third Evacuation	21.7	133.1	70.4	20.2	239.5	76.4	20.2	236.2	77.6	Wednesday, 11:00 AM.		
Temperature, T <sub>1</sub> °	30.3	132.3	81.7	2.0	239.5	81.6	2.0	236.2	82.1	Wednesday, 3:00 PM.		
Temperature, T <sub>2</sub> °	47.1	131.0	99.2	3.8	239.5	99.8	3.2	236.2	98.5	Wednesday, 9:15 PM.		
Temperature, T <sub>3</sub> °	61.0	130.3	109.1	6.2	239.5	110.5	4.9	236.2	108.7	Thursday, 8:30 AM.		
First Expansion	58.1	130.3	108.8	58.0	239.5	110.0	0.8	236.2	108.5	Thursday, 2:00 PM.		
Second Expansion	56.2	130.4	108.5	56.1	..	109.5	56.3	236.2	108.1	Thursday, 4:15 PM.		
Stop	24.9	132.7	76.8	6.1	239.5	76.3	5.5	236.2	77.2	Friday, 10:00 AM.		

TABLE 13 VAPOR PRESSURE RUNS (6 of 8)

Supporting Acid Analyses												
Run No.	Sample	Phys. Appear.	wt %					ppm (w/w)				
			HNO <sub>3</sub>	NO <sub>2</sub>	H <sub>2</sub> O	PF <sub>5</sub>	M <sub>2</sub> O <sub>3</sub>	Fe	Cr	Ni	Al	Comments
6	Stock Solution - 6	Clear	Bal.	47.4	0.4	0.73	<0.01	1	<1	<1	<1	High NO <sub>2</sub> Low H <sub>2</sub> O High PF <sub>5</sub>
	Pre Test	Clear		47.0	0.4							169.0 gm loaded at 39 °F (3.9 °C) ≡ 101.9 cm <sup>3</sup>
	Post Test	Clear		44.2	0.4							
	Residual Acid	Clear		44.3	0.4	0.72		2	<1	<1	<1	137.5 gm recovered
PVT Data												
Step	Test Vessel No. 1				Test Vessel No. 2				Test Vessel No. 3			
	P <sub>1</sub> "Hg	V <sub>1</sub> cm <sup>3</sup>	T <sub>1</sub> °F	P <sub>2</sub> "Hg	V <sub>2</sub> cm <sup>3</sup>	T <sub>2</sub> °F	P <sub>3</sub> "Hg	V <sub>3</sub> cm <sup>3</sup>	T <sub>3</sub> °F	Comments		
Start	34.9	132.9	74.0	0.2	239.5	76.2	<0.1	236.2	77.4	Monday, 11:00 AM		
First Evacuation	24.2	132.9	73.2	23.1	239.5	76.9	23.0	236.2	77.7	Monday, 11:15 AM.		
Second Evacuation	23.4	133.0	72.1	21.2	239.5	76.7	21.2	236.2	78.3			
Third Evacuation	22.5	133.1	71.1	21.0	239.5	76.6	21.0	236.2	77.8	Monday 11:30 AM.		
Temperature, T <sub>1</sub> °	29.0	132.5	79.8	1.8	239.5	79.6	1.5	236.2	80.3	Monday, 2:30 PM.		
Temperature, T <sub>2</sub> °	44.2	131.3	95.6	2.9	239.5	96.1	2.6	236.2	96.1	Monday, 9:30 PM.		
Temperature, T <sub>3</sub> °	60.8	130.4	108.1	5.0	239.5	109.4	4.1	236.2	108.6	Tuesday, 9:15 AM.		
First Expansion	57.3	130.4	108.4	57.2	239.5	108.7	0.6	236.2	108.1	Tuesday, 2:00 PM.		
Second Expansion	56.1	130.4	107.7	56.0	239.5	108.8	56.1	236.2	108.3	Tuesday, 4:45 PM.		
Stop	25.0	132.7	77.1	<0.1	239.5	76.4	<0.1	236.2	77.3	Wednesday, 8:45 AM.		

TABLE 13. VAPOR PRESSURE RUNS (7 of 8)

Supporting Acid Analyses												
Run No.	Sample	Phys. Appear.	wt %					ppm (w/w)				
			HNO <sub>3</sub>	NO <sub>2</sub>	H <sub>2</sub> O	PF <sub>5</sub>	M <sub>2</sub> O <sub>3</sub>	Fe	Cr	Ni	Al	Comments
2	Stock Solution - 7	Clear	Bal.	47.4	1.0	0.52	<0.01	<1	<1	<1	<1	High NO <sub>2</sub> - High H <sub>2</sub> O - Low PF <sub>5</sub> .
	Pre Test	Clear	..	47.4	1.0	..	..	..	..	..	..	165.5 gm loaded at 37.0°F (2.8°C) ≡ 99.8 cm <sup>3</sup> .
	Post Test	Clear	..	42.2	1.0	..	..	..	..	..	..	
	Residual Acid	Clear	Bal.	43.1	1.0	0.55	<0.01	3	<1	<1	<1	134.4 gm recovered.
PVT Data												
Step	Test Vessel No. 1			Test Vessel No. 2			Test Vessel No. 3			Comments		
	P <sub>1</sub> "Hg	V <sub>1</sub> cm <sup>3</sup>	T <sub>1</sub> °F	P <sub>2</sub> "Hg	V <sub>2</sub> cm <sup>3</sup>	T <sub>2</sub> °F	P <sub>3</sub> "Hg	V <sub>3</sub> cm <sup>3</sup>	T <sub>3</sub> °F			
Start	34.4	135.0	72.8	0.2	239.5	76.8	< 0.1	236.2	78.4	Monday, 2:05 PM.		
First Evacuation	24.8	135.0	72.4	22.9	239.5	77.1	22.8	236.2	77.8			
Second Evacuation	24.0	135.1	71.6	21.9	239.5	76.8	21.8	236.2	77.8			
Third Evacuation	23.0	135.1	70.8	21.2	239.5	76.8	21.1	236.2	77.9	Monday, 2:20 PM.		
Temperature, T <sub>1</sub> °	29.0	134.6	78.8	1.6	239.5	78.7	1.1	236.2	79.4	Monday, 5:30 PM.		
Temperature, T <sub>2</sub> °	46.2	133.3	96.7	2.8	239.5	98.6	1.8	236.2	97.7	Monday, 9:30 PM.		
Temperature, T <sub>3</sub> °	66.2	132.2	111.8	5.5	239.5	113.2	3.1	236.2	111.6	Tuesday, 8:45 AM.		
First Expansion	63.3	132.2	111.6	63.2	239.5	113.2	0.1	236.2	111.7	Tuesday, 1:30 PM.		
Second Expansion	62.3	132.2	111.5	62.1	239.5	113.3	62.0	236.2	111.8	Tuesday, 3:30 PM.		
Stop	..	..	..	..	239.5	..	..	236.2	..	Wednesday, 8:30 AM.		



TABLE 13 VAPOR PRESSURE RUNS (8 of 8)

Supporting Acid Analyses													
Run No.	Sample	Phys. Appearance	wt %					ppm (w/w)					Comments
			HNO <sub>3</sub>	NO <sub>2</sub>	H <sub>2</sub> O	PF <sub>5</sub>	M <sub>2</sub> O <sub>3</sub>	Fe	Cr	Ni	Al		
8	Stock Solution - 8	Clear	Bal.	47.2	1.0	0.73	<0.01	1	<1	<1	<1	High NO <sub>2</sub> - High H <sub>2</sub> O - High PF <sub>5</sub>	167.0 gm loaded at 33.0° F (0.6° C) ≡ 100.4 cm <sup>3</sup> .
	Pre Test	Clear	..	47.0	1.0	..	..	..	..	..	..		
	Post Test	Clear	..	43.1	1.0	..	..	..	..	..	..		
	Residual Acid	Clear	..	43.1	1.0	0.70	..	3	<1	<1	<1	140.0 gm recovered	
PVT Data													
Step	Test Vessel No. 1				Test Vessel No. 2				Test Vessel No. 3				Comments
	P <sub>1</sub> "Hg	V <sub>1</sub> cm <sup>3</sup>	T <sub>1</sub> °F	P <sub>2</sub> "Hg	V <sub>2</sub> cm <sup>3</sup>	T <sub>2</sub> °F	P <sub>3</sub> "Hg	V <sub>3</sub> cm <sup>3</sup>	T <sub>3</sub> °F				
Start	36.2	134.2	71.0	0.2	239.5	75.4	< 0.1	236.2	74.4	Monday, 10:45 AM.			
First Evacuation	23.2	134.2	70.4	22.0	239.5	76.0	21.9	236.2	75.2				
Second Evacuation	22.2	134.3	<70.0	20.8	239.5	76.0	20.8	236.2	75.0				
Third Evacuation	21.8	134.3	<70.0	20.0	239.5	76.0	20.0	236.2	75.0	Monday, 11:00 AM.			
Temperature, T <sub>1</sub> <sup>o</sup>	31.0	133.5	81.4	2.6	239.5	81.7	2.1	236.2	81.3	Monday, 4:00 PM.			
Temperature, T <sub>2</sub> <sup>o</sup>	44.4	132.4	95.6	4.0	239.5	95.4	3.0	236.2	96.2	Monday, 9:30 PM.			
Temperature, T <sub>3</sub> <sup>o</sup>	56.3	131.7	105.5	6.4	239.5	105.0	4.4	236.2	105.9	Tuesday, 9:30 AM.			
First Expansion	54.2	131.7	105.5	54.1	239.5	104.9	0.4	236.2	105.7	Tuesday, 4:00 PM.			
Second Expansion	53.2	131.7	105.6	53.0	239.5	105.2	53.1	236.2	106.0	Tuesday, 6:45 PM.			
Stop	25.0	133.9	75.6	8.2	239.5	75.7	9.3	236.2	75.0	Wednesday, 8:45 AM.			

in keeping with the accuracy of the method. The ranges of concentration of phosphorous pentafluoride at the two levels tested were 0.52-0.57 wt %, at the low level, and 0.70-0.74 wt %, at the high level. The values shown in the test matrix were rounded off to 0.5 and 0.7 wt %, respectively. Iron content of the acid increased a few parts per million during the test because of attack on the probes, in test vessel  $V_1$ , for measuring temperature and pressure. The magnitude of attack would not effect PVT data. Each stock solution was analyzed completely before the test. Complete analyses were usually performed post test as well. Nitrogen dioxide, water and phosphorous pentafluoride contents were always determined, and were found unchanged. In some cases, post test analyses for metal oxides and aluminum were waived, because constant levels were predictable.

With reference to PVT data, it will be noted that relatively large differences were recorded between the temperatures of the test vessel containing acid and the two vessels under vacuum. The acid was relatively cold, but the residual gas in the other two vessels was near room temperature. The differences were accentuated during the evacuation steps performed to rid test vessel  $V_1$  of residual nitrogen before commencing measurements of pressure at elevated temperatures. The acid cooled down during evacuation, as expected. It took several hours, from the time heat was applied, for the acid to reach a given test temperature. During this time, the differences in temperature readings between the probes decreased. Such variations as were recorded fall within the accuracy of the measurement. Highest reliance is placed in readings from the probe immersed in the liquid. There was an increase in pressure for test vessel  $V_1$  with each increase in temperature. Except on occasions when readings were taken before thermal equilibrium was fully established, the increases in pressure with temperature were highly regular. When acid vapors were expanded into test vessels  $V_2$  and  $V_3$ , an immediate drop in pressure and temperatures were noted for test vessel  $V_1$ . Temperature gradually rose to its original value, and at this point, pressure and temperature readings were taken for each test vessel. Close agreement was noted for the pressure readings for all test vessels involved in the expansion steps. The test vessels were allowed to cool to room temperature after stable readings were obtained following the second evacuation. The process required several hours. To reduce subsequent outgassing effects, acid vapors in test vessels  $V_2$  and  $V_3$  were re-evacuated. A slight rise in pressure, evident by the time the experiment was terminated, testified to the value of this step. Normally, the temperature and pressure for test vessel  $V_1$  were recorded to provide another, low temperature data point.

As had been done for Experiment 2, pressure readings for test vessel  $V_1$  at temperatures  $T_1^\circ$ ,  $T_2^\circ$  and  $T_3^\circ$  were converted to psia and plotted as equilibrium pressure as a function of temperature. Pressure readings at 80, 90 and 100°F (26.7, 32.2 and 37.8°C) were read from the curves and tabulated in the two-cube factorial test matrix. Pressure readings at  $T_3^\circ$  were converted to atmospheres, and similarly tabulated. These tables will be considered presently. The following are specific comments for each of the eight vapor pressure runs.

Data for the vapor pressure run with stock solution 1 are shown on page 1 of Table 13. Results from chemical analyses and PVT data were normal in every respect. A plot of pressure as a function of temperature appears in Figure 9. The legend indicates that the stock solution contained low concentrations of nitrogen dioxide, water and phosphorous pentafluoride. This curve serves as a basis for evaluating data for the rest of the stock solutions in the test matrix. The pressure recorded on test termination was approximately one psia below the curve. This corresponds to a loss of some nitrogen dioxide from the liquid during the expansion steps. The decrease in pressure readings for test vessel  $V_1$  at  $T_3^\circ$  during the expansion steps, reveals the presence of a vapor pressure and a decomposition component for equilibrium pressure, as measured prior to the expansion steps.

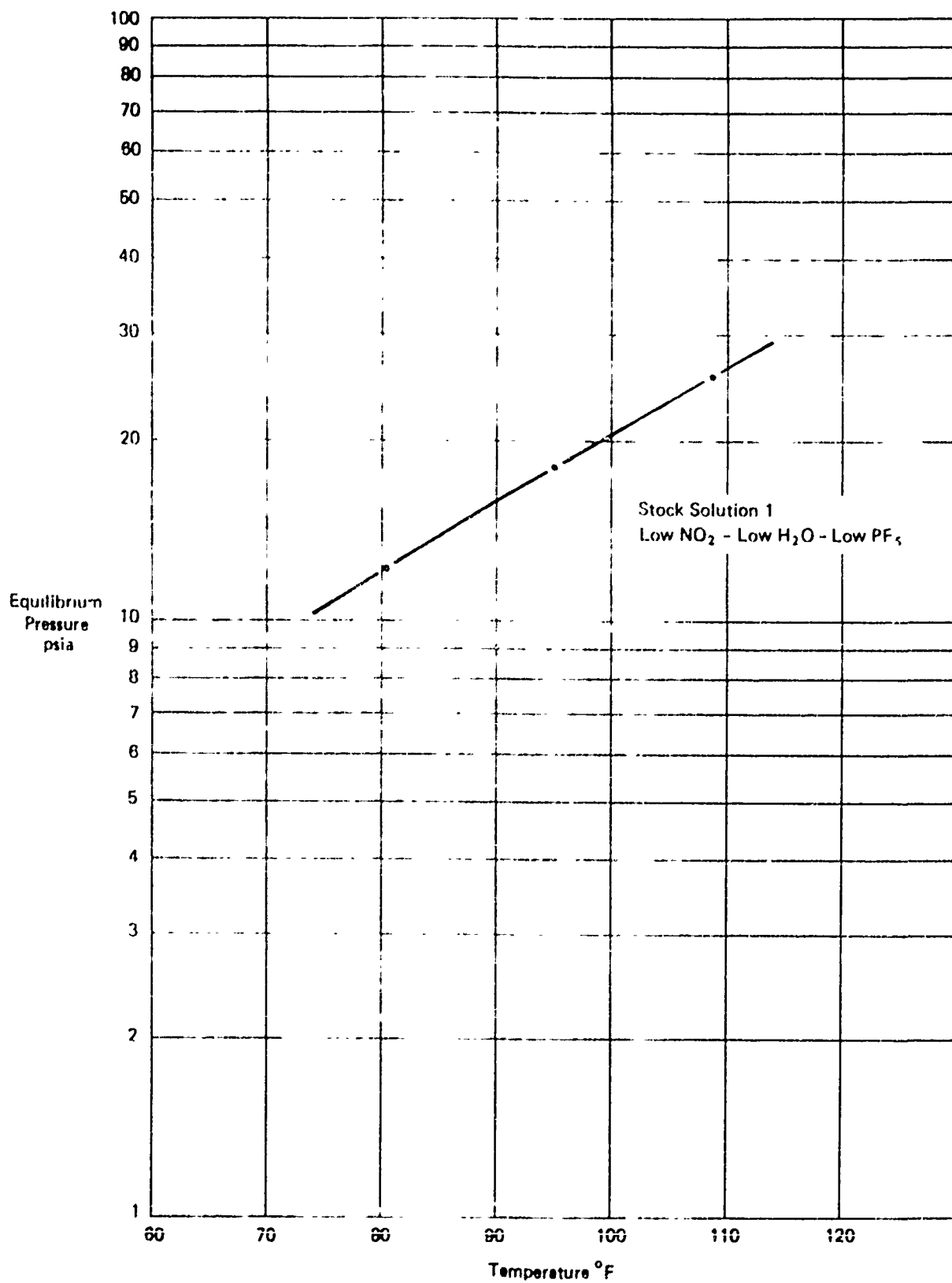


Figure 9. Vapor Pressure Run, Stock Solution 1

Data for the vapor pressure run with stock solution 2 are shown on page 2 of Table 13. Chronologically, this was the seventh run made. On the basis of the low value for iron content of the acid sample post test, and the results from analyses in support of preceding runs, analyses for the metal oxides and aluminum content of the residual acid removed from test vessel  $V_1$  after the run were waived. A plot of temperature versus pressure for this run is shown in Figure 10. The chemical analyses, PVT data, and the vapor pressure curve all appear normal.

Data for the vapor pressure run with stock solution 3 are given in Table 13, page 3. All data appear normal. A plot of temperature versus pressure appeared in Figure 8 and is also shown in Figure 11. The former figure showed the increase in pressure at a given temperature with an initially higher concentration of nitrogen dioxide. The latter is the curve for stock solution 3 alone. The pressure reading obtained at the end of the run with stock solution 3 falls below the curves in both figures, due to loss of nitrogen dioxide during the expansion steps.

Data for the vapor pressure run with stock solution 4 are given in Table 13, page 4, and Figure 12. Although the data are reliable, they do not fit directly into the test matrix. As shown by the supporting analyses, stock solution 4 contained approximately one percent more nitrogen dioxide than the other three stock solutions with relatively low nitrogen dioxide content. The presence of excess nitrogen dioxide is also evident from the position of the curve in Figure 12. It lies approximately one psia higher than the rest of this family of curves represented by Figures 9-12.

Data for the vapor pressure run with stock solution 5 are given in Table 13, page 5, and Figure 13. For reasons previously described, analyses of residual acid for metal oxides and aluminum contents were waived. All of the data reported appear normal.

Data for the vapor pressure run with stock solution 6 are given in Table 13, page 6, and Figure 14. All of the data appear normal. Only the analysis of residual acid for metal oxides content was waived. Aluminum content was determined as a precautionary measure.

Data for the vapor pressure run with stock solution 7 are given in Table 13, page 7, and Figure 15. Results of chemical analyses in support of the run are considered reliable. PVT data obtained likewise appear acceptable. A thermistor lead was broken during post test manipulations and readings at the end of the run were waived to expedite repairs. A relatively large loss in nitrogen dioxide resulted because the post test sampling and analysis steps were performed at a relatively high temperature.

Data for the vapor pressure run with stock solution 8 are given in Table 13, page 8, and Figure 16. The chemical analyses and PVT data reported are reliable, but three points deserve mention. A relatively large loss of nitrogen dioxide was indicated by post test analyses. Most of this loss is attributed to post test sampling and analysis steps. Since analytical results appeared normal in other respects, analyses of the residual acid for metal oxides and aluminum content were waived. PVT data are incomplete in that the acid temperature fell below the limit of the recorder during evacuation steps performed to remove residual nitrogen from test vessel  $V_1$  at the beginning of the run. For this reason, temperature is reported as less than 70°F at one point in Table 13.

Upon completion of the vapor pressure measurements, data were taken from Figures 9-16 to construct Table 14. Specifically, values were read from the graphs at 80, 90 and 100°F (26.7, 32.2 and 37.8°C), corresponding to the pressure ( $P_1$ ) in test vessel  $V_1$ , at each of these temperatures, for each of the stock solutions. The composition of each stock solution is given in relative terms, e.g., concentration of nitrogen dioxide ( $[NO_2]$ ), low. Taken together, these relative data display

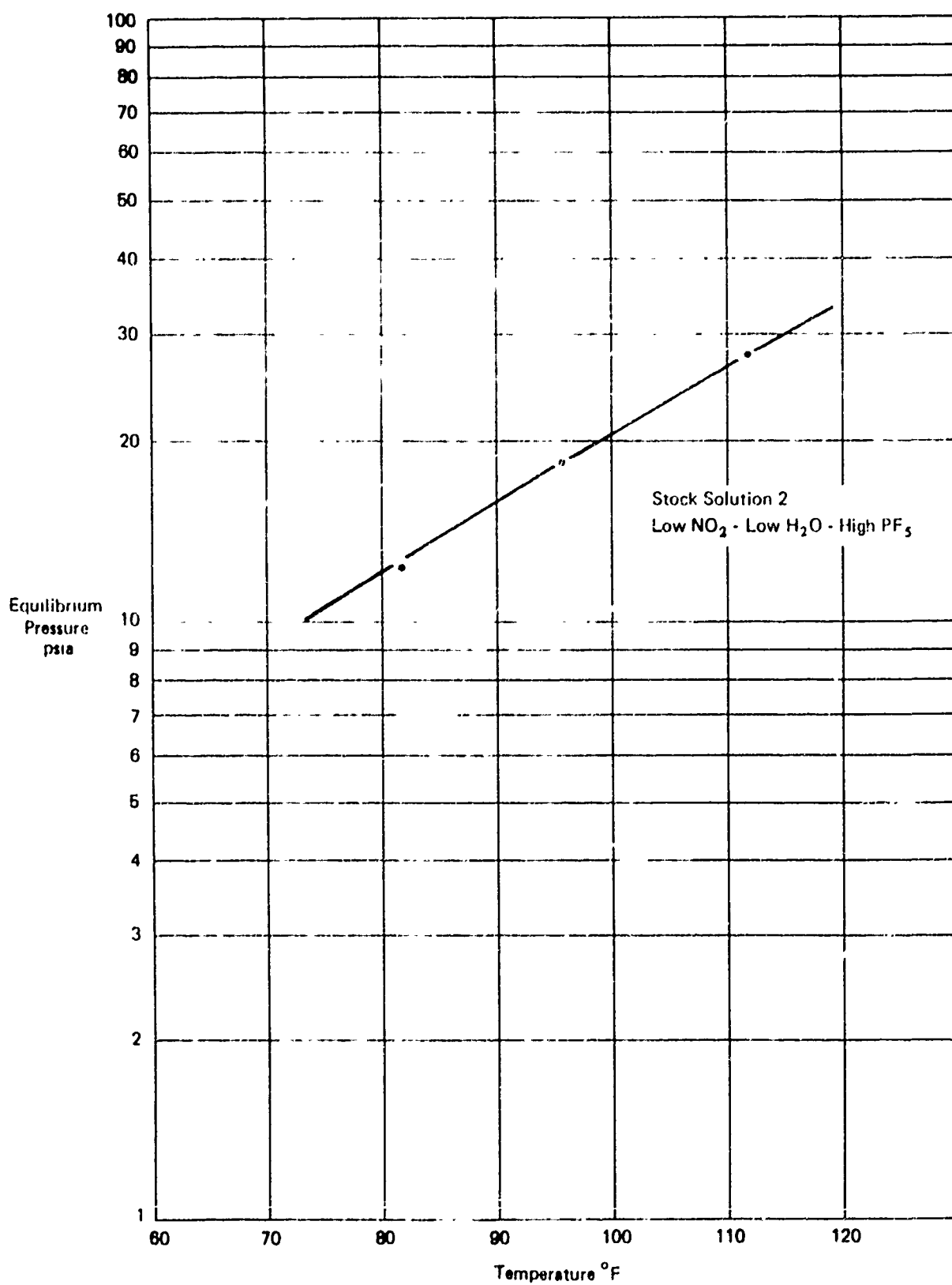


Figure 10 Vapor Pressure Run, Stock Solution 2

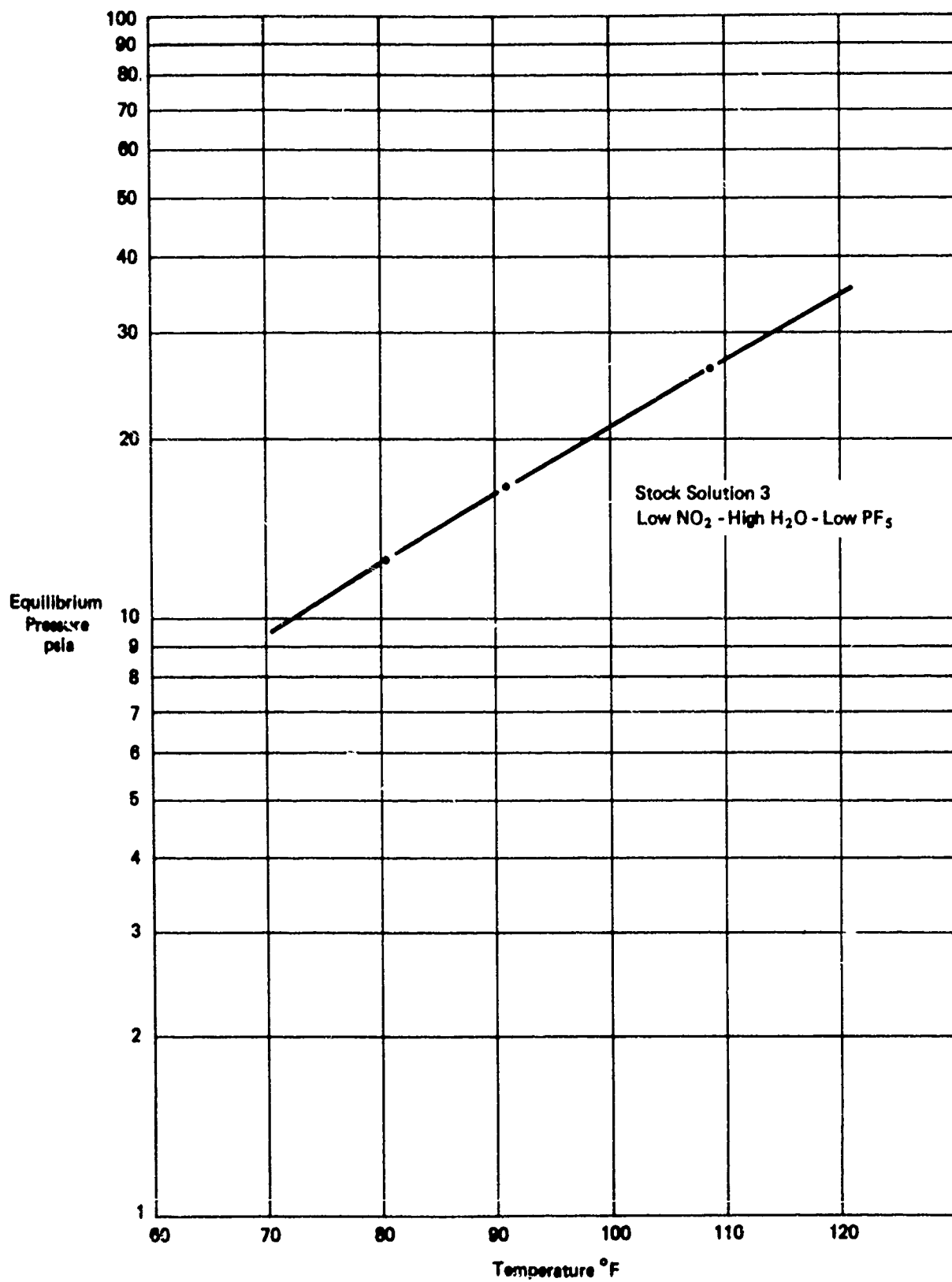


Figure 11. Vapor Pressure Run, Stock Solution 3

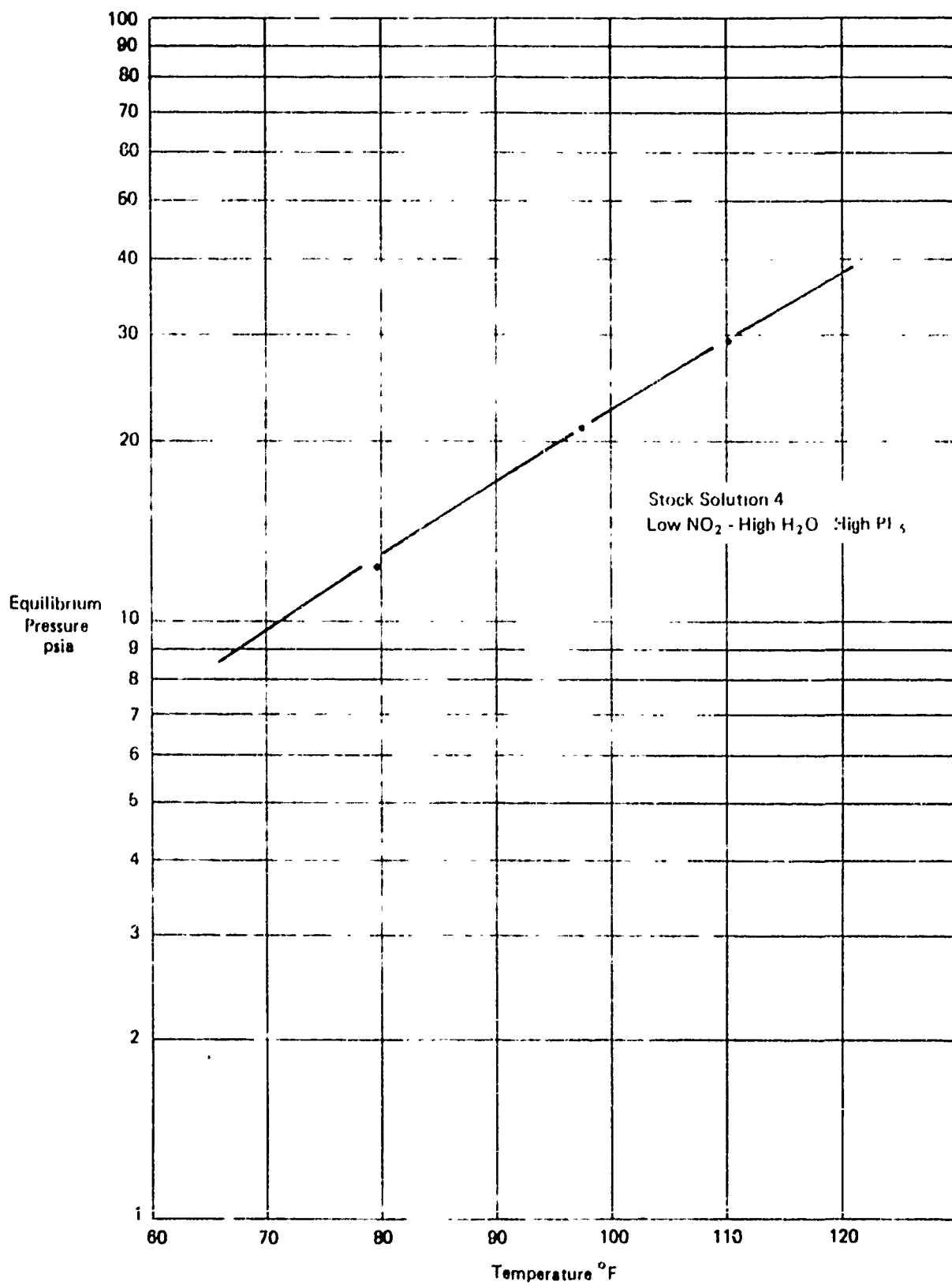


Figure 12. Vapor Pressure Run, Stock Solution 4

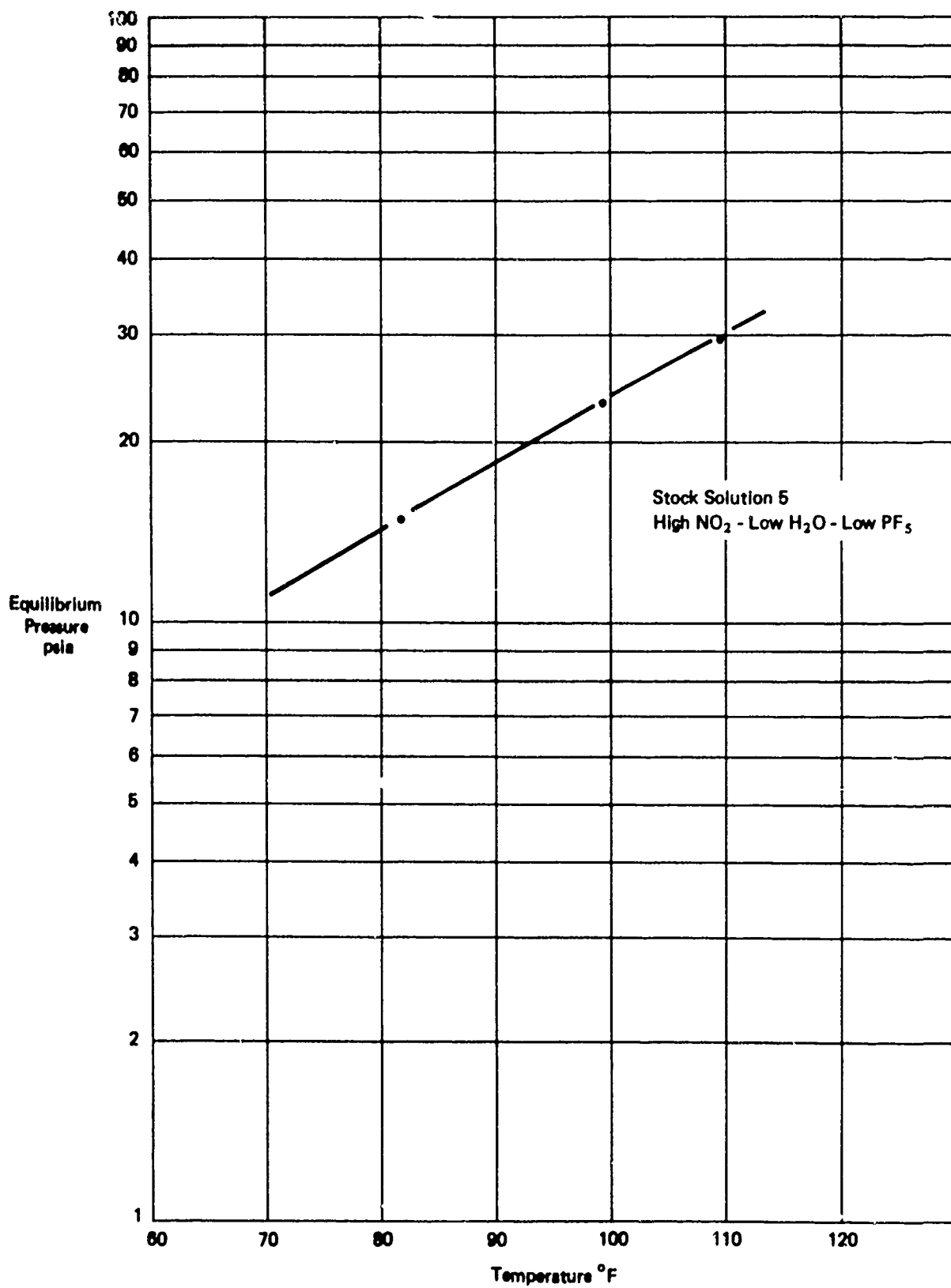


Figure 13. Vapor Pressure Run, Stock Solution 5



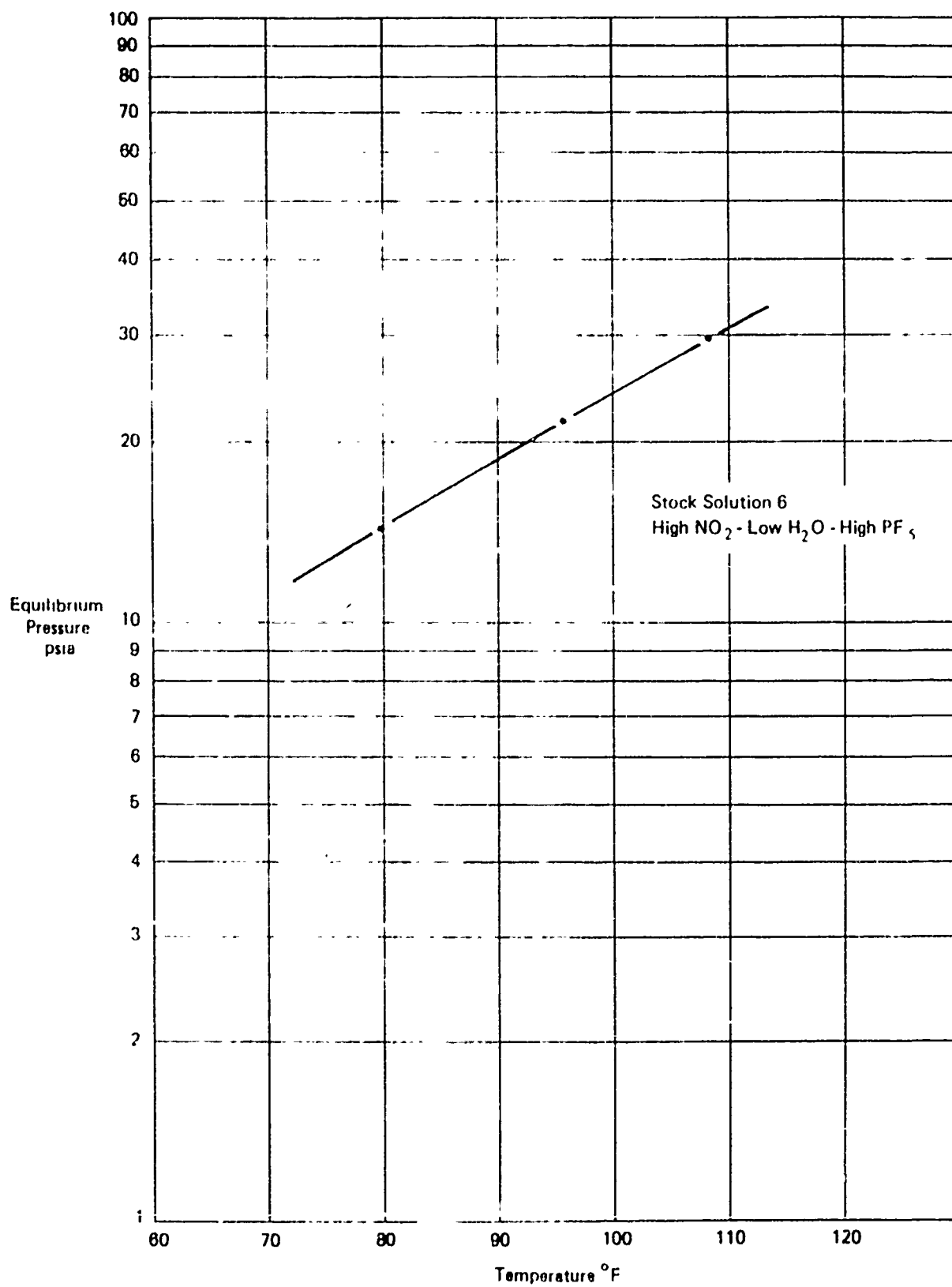


Figure 14 Vapor Pressure Run, Stock Solution 6

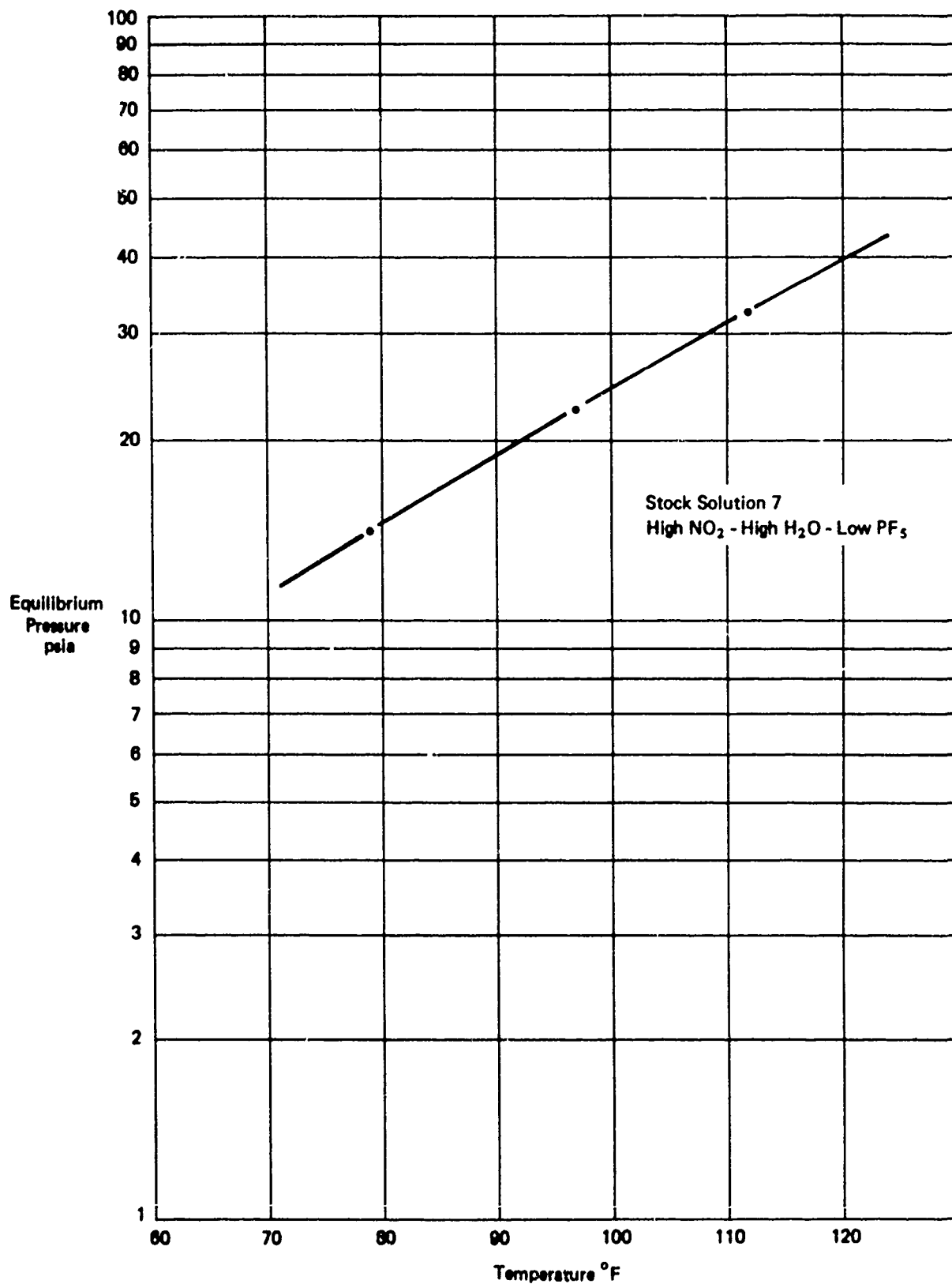


Figure 15. Vapor Pressure Run, Stock Solution 7

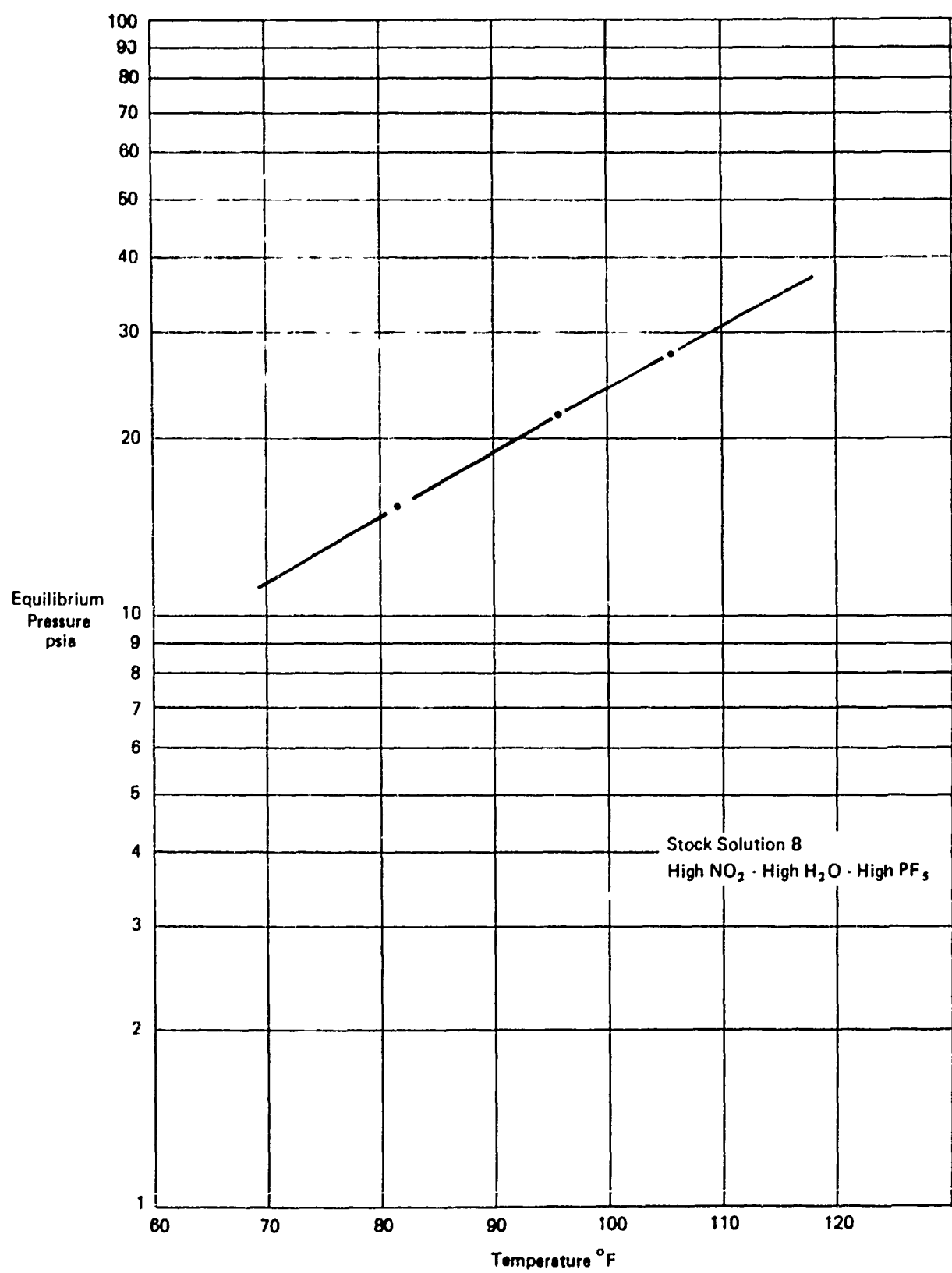


Figure 16. Vapor Pressure Run, Stock Solution 8

TABLE 14. MODIFIED HDA PRESSURE VERSUS TEMPERATURE AT CONSTANT VOLUME

Stock Solution	Test Matrix			$P_1$ psia	$T^\circ$ $^\circ\text{F}$	$P_1$ psia	$T^\circ$ $^\circ\text{F}$	$P_1$ psia	$T^\circ$ $^\circ\text{F}$	Comments
	$[\text{NO}_2]$	$[\text{H}_2\text{O}]$	$[\text{PF}_5]$							
1	Low	Low	Low	12.0	80	15.7	90	20.5	100	Run No. 4
2	Low	Low	High	12.0	80	15.7	90	20.5	100	Run No. 7
3	Low	High	Low	12.3	80	16.1	90	21.0	100	Run No. 1
4	Low	High	High	12.9	80	17.1	90	22.5	100	Run No. 3
5	High	Low	Low	14.3	80	18.5	90	23.8	100	Run No. 5
6	High	Low	High	14.3	80	18.6	90	23.9	100	Run No. 6
7	High	High	Low	14.5	80	18.8	90	24.3	100	Run No. 2
8	High	High	High	14.6	80	18.8	90	24.2	100	Run No. 8

the 2-cube factorial test matrix. The sequence in which the vapor pressure runs were made is noted under comments. Inspection of the table reveals at a glance that nitrogen dioxide is a controlling variable for vapor pressure. Further analysis of the data will be found in Part III, Technical Discussion.

Table 15 was constructed from pressure readings ( $P_1$ ) for test vessel  $V_1$  in Table 13, before and after the expansions carried out at the highest test temperature ( $T_3^\circ$ ) to which each stock solution was exposed. Representation of the 2-cube factorial test matrix is the same as in Table 14. Pressures and changes in pressure ( $\Delta P_1$ ) for test vessel  $V_1$  are expressed in atmospheres, as are the sums of the pressure drops ( $\Sigma \Delta P_1$ ) for the two expansions, for each stock solution. It is immediately evident that a decrease in pressure followed each expansion with each stock solution. This proves that a decomposition pressure component is part of the equilibrium pressures measured as a function of temperature. Calculation of the magnitude of the decomposition pressure is considered in Part III, Technical Discussion. Data from the run with stock solution 3 were not used in the calculation, because pressure readings after the first expansion were taken before thermal equilibrium was established. Variations in  $\Delta P$  for the other stock solutions reflect the accuracy of temperature and pressure measurements. The relative constancy ( $0.14 \pm 0.03$  atm) for total pressure drop is explained by the similar compositions of the stock solutions.

TABLE 15. MODIFIED HDA PRESSURE VERSUS VOLUME AT CONSTANT TEMPERATURE

Stock Solution	Test Matrix			$T_3^\circ$ $^\circ\text{F}$	$P_1$ Atm	First Expansion			Second Expansion			$\Sigma \Delta P_1$
	$[\text{NO}_2]$	$[\text{H}_2\text{O}]$	$[\text{PF}_5]$			$T^\circ\text{F}$	$P_1$ Atm	$\Delta P_1$	$T^\circ\text{F}$	$P_1$ Atm	$\Delta P_1$	
1	Low	Low	Low	108.7	1.74	108.0	1.64	0.10	108.1	1.60	0.04	0.14
2	Low	Low	High	111.6	1.86	111.2	1.77	0.09	111.0	1.73	0.04	0.13
3	Low	High	Low	108.5	1.77	109.9	1.76	0.01	108.4	1.67	0.08	0.09
4	Low	High	High	111.0	1.97	109.4	1.64	0.13	109.2	1.60	0.04	0.17
5	High	Low	Low	109.8	2.03	108.8	1.94	0.09	108.5	1.87	0.07	0.16
6	High	Low	High	108.1	2.03	108.4	1.91	0.12	107.7	1.87	0.04	0.16
7	High	High	Low	111.8	2.21	111.6	2.11	0.10	111.5	2.08	0.03	0.13
8	High	High	High	105.5	1.88	105.5	1.81	0.07	105.6	1.77	0.04	0.11

## 2.0 TASK 2 - SOLUBILITY TESTS

### 2.1 Corrosion Product Solubility Tests

High Density Acid containing particles of corrosion products would overtax the capacity of on-board filters and affect propulsion system performance. Quantitative data for the solubility of corrosion products as functions of temperature and propellant composition are needed to set limits for successful propulsion system operation. For a variety of reasons, solubility data previously reported are open to question. Experiments were undertaken to provide more reliable data.

The first experiments were performed to perfect the experimental procedure to be used for quantitative studies of Modified HDA and Standard HDA solutions contaminated, through contact with aluminum and stainless steel alloys, with naturally formed corrosion products. The final procedure consisted of filtering a given, turbid solution at a preselected temperature, through a set of inert membranes, with different pore sizes. The clear filtrates obtained were analyzed by standard procedures to determine the concentration of metals present. A decrease in the concentration of the metals after filtration was related to corrosion product solubility.

The type of filtration equipment developed to perform solubility tests is depicted in Figure 17. On the left side of the figure are shown the parts of a commercially available pressure filter and a set of Teflon membranes. The assembled filter, installed in a simulated polyethylene flask containing a Teflon receiver, is shown on the right side of the figure. A pressure filter was chosen because it provided a seal which prevented particles from bypassing the membranes and interfering with analysis of the filtrate by atomic absorption spectroscopy. Sufficient nitrogen pressure was applied to cause a reasonably rapid flow rate, but the pressure drop was never more than would be experienced during conventional filtration under vacuum. The metal parts of the filter were reportedly made of 304 stainless steel, and were certified as such by spectroscopic analysis of the reservoir.

Between tests with contaminated acids, a number of filtrations were made with pure acid, in order to determine the degree of attack on the filter, and the corresponding contamination of the filtrates. Filtration parameters were the same for the pure and contaminated acids. The results from these tests are given in Table 16. It lists the type of contaminated acid used before a series of tests with a given type of pure HDA. The composition of the pure acids is included in Table 17, which includes the analyses for all the pure stock solutions prepared for use in solubility tests. Preparation and analysis were by standardized procedures. The comment in Table 16, Series Tests, indicates that the same type of contaminated HDA had been used previously, as the type of pure HDA currently being studied. A difference between the types of contaminated and pure acids studied is indicated by the comment, Parallel Tests. The attack on the filter is shown in terms of the difference in the iron content of the acid tested, before and after filtration. The effect of switching from one type of acid to another is relatively large, as can be seen from the average change in iron content for a given series of tests.

The results from the filtration tests with pure HDA were used to correct measured values for iron concentration in a given filtrate. Reductions of one or two ppm were made, depending on the type of HDA filtered, and the type of HDA previously filtered.

The final step in procedure development consisted of filtering aliquots of Standard HDA through Teflon membranes of different pore size, and in different combinations of pore size. The object was to certify the plan to use a set of four membranes with pore sizes of: 5.0, 3.0, 1.0 and 0.2 $\mu$  (micron). The membrane with the largest pore size was to be on top of the pack, toward in-

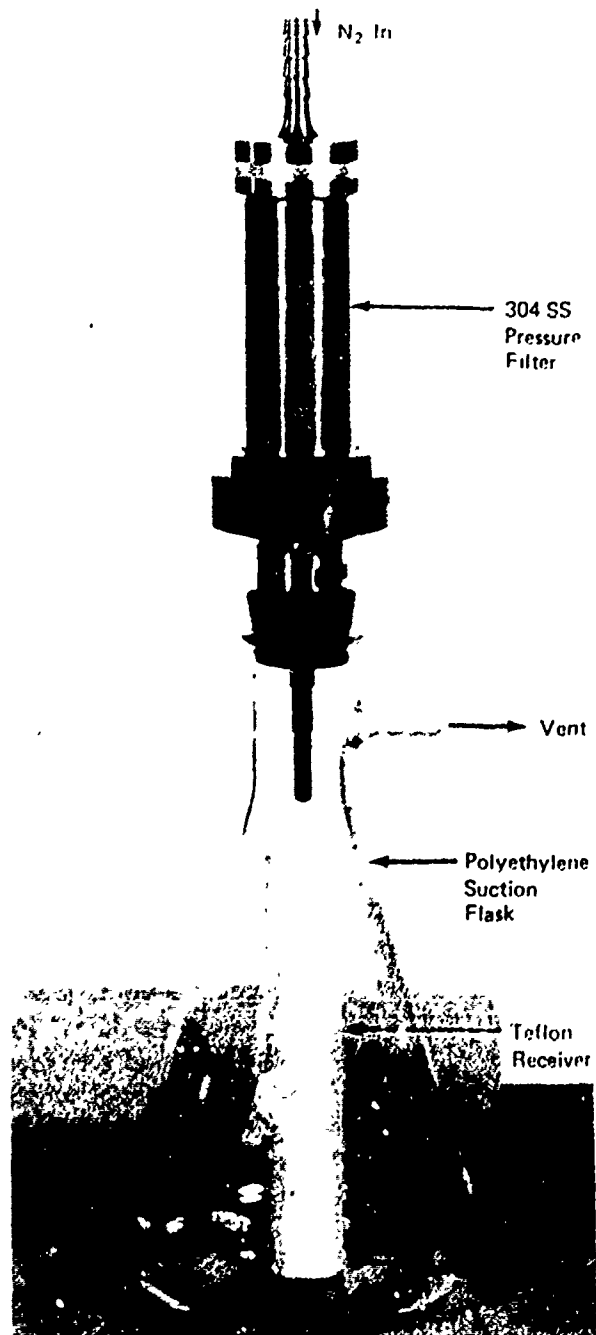
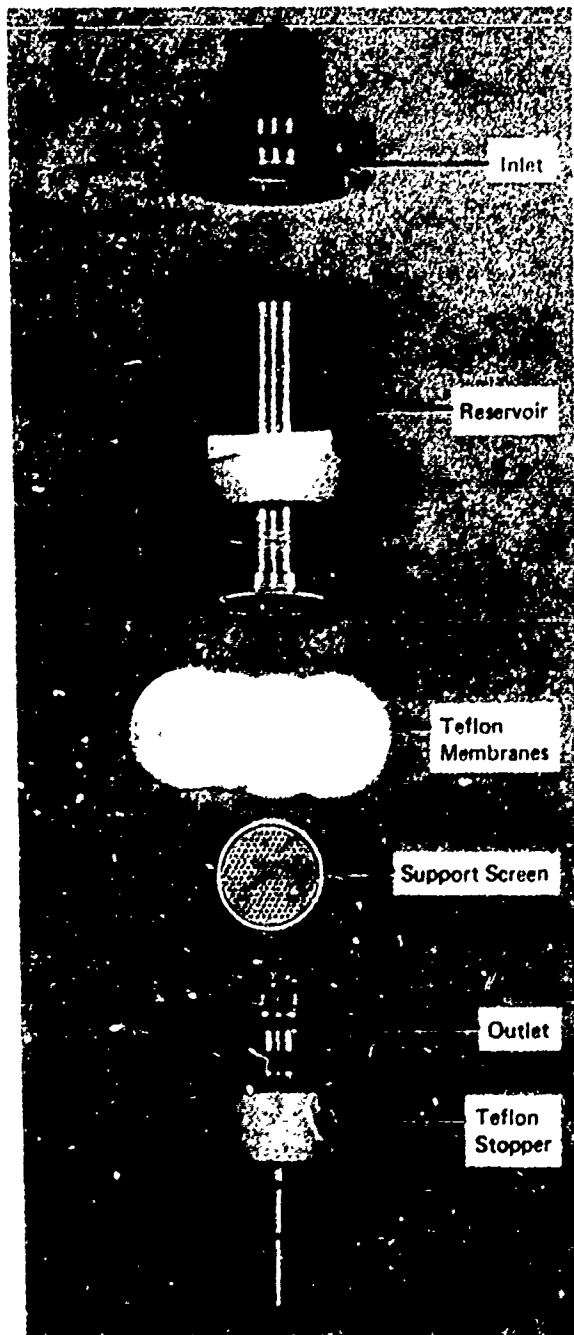


Figure 17. HDA Filtration Equipment

TABLE 16. PRELIMINARY SOLUBILITY TESTS - FILTER COMPATIBILITY

Test No.	Series	Type HDA Tested	Type HDA Used previously	Increase in Fe ppm (w/w)	Avg. $\Delta$ Fe ppm (w/w)	Comments
1	A	Modified	Modified	0.5	--	Series Tests - Acid No. 77-17.
2	A	Modified	Modified	0.0	--	
3	A	Modified	Modified	0.8		
4	A	Modified	Modified	0.8		
5	B	Modified	Standard	0.5	0.5	Parallel Tests - Acid No. 77-18
6	B	Modified	Standard	1.5		
7	B	Modified	Standard	1.2		
8	C	Standard	Standard	1.2	1.1	Series Tests - Acid No. 77-18.
9	C	Standard	Standard	1.9		
10	D	Standard	Modified	2.1	1.1	
11	D	Standard	Modified	1.2		Parallel Tests - Acid No. 77-17.
	D	Standard	Modified	--	1.7	

TABLE 17. PURE STOCK SOLUTIONS FOR SOLUBILITY TESTS

Stock No.	Physical Appearance	wt %					ppm (w/w)				Comments
		HNO <sub>2</sub>	NO <sub>2</sub>	H <sub>2</sub> O	Cl	M <sub>2</sub> O <sub>3</sub>	Fe	Cr	Ni	Al	
77-17	Clear	Bal.	43.4	0.5	0.7	0.0003	< 1	< 1	< 1	< 1	Standard HDA.
77-18	Clear	Bal.	43.4	0.5	0.6	0.0004	< 1	< 1	< 1	< 1	Modified HDA.
77-19	Clear	Bal.	43.2	0.3	0.6	0.0008	< 1	< 1	< 1	< 1	Modified HDA.

coming acid. The results of these experiments are shown in Table 18. The table is arranged to show the type of HDA tested, the filter membranes employed, pre and post test temperatures, to the nearest degree, acid composition before and after filtration, filtration pressure, acid flow rate, the weight of particulate matter collected on each membrane, and pertinent comments. In each case, a 50 cm<sup>3</sup> aliquot of Standard HDA which had deteriorated in quality during extended exposure to a stainless steel tank and an aluminum alloy drum was filtered at room temperature. The designation OK signifies that before test the acid contained a few small, visible particles. These were removed during filtration. No flow was noted for membranes as received until the pore size of the membrane being tested was  $\geq 1\mu$  (equal or greater than one micron). However, flow could be induced through smaller pores if the membranes were conditioned with CH<sub>2</sub>Cl<sub>2</sub> (methylene chloride). Test No. 8 included prefiltration with 50 cm<sup>3</sup> of this solvent. Subsequent tests involved merely wetting the membranes immediately before exposing them to HDA.

Since Test No. 8 appeared normal in all respects, analyses of the filtrate and determination of particulate matter were carried out. Chemical analyses proved that an acceptably small amount of nitrogen dioxide was lost during filtration. Therefore, solubility data can be reviewed in terms of the composition of the acid at the start of the filtration. There was no change in water content, proving that all transfers had been carried out satisfactorily. Atomic absorption analyses showed a

TABLE 18. PRELIMINARY SOLUBILITY TESTS - FILTER MEMBRANE SELECTION

Test No.	Type HDA and CPs	Membranes		Acid-Start										Filtrate										Flow Rate cm <sup>3</sup> /min	Comments	
		μ	No.	Temp.	Phys. Appear.	wt %		ppm (w/w)				H <sub>2</sub> Press. psig	Temp.	Phys. Appear.	wt %		ppm (w/w)				Particulate gm/100 cm <sup>3</sup>					
						°F	°C	NO <sub>2</sub>	H <sub>2</sub> O	Fe	Cr				Ni	Al	NO <sub>2</sub>	H <sub>2</sub> O	Fe	Cr		Ni	Al			
1	Sol.-SS/Al	0.2	2	75	24	OK	34.3	0.7	35	10	11	52	12	..	..	..	..	..	..	..	..	..	..	No Flow	50 cm <sup>3</sup> Aliquots.	
2	Sol.-SS/Al	0.2	1	75	24	OK	34.3	0.7	35	10	11	52	12	..	..	..	..	..	..	..	..	..	..	No Flow		
3	Sol.-SS/Al	0.5	1	75	24	OK	34.3	0.7	35	10	11	52	12	..	..	..	..	..	..	..	..	..	..	No Flow		
4	Sol.-SS/Al	1.0	2	75	24	OK	34.3	0.7	35	10	11	52	12	..	..	..	..	..	..	..	..	..	..	No Flow		
5	Sol.-SS/Al	1.0	1	75	24	OK	34.3	0.7	35	10	11	52	12	..	..	..	..	..	..	..	..	..	..	2		
6	Sol.-SS/Al	3.0	1	75	24	OK	34.3	0.7	35	10	11	52	12	..	..	..	..	..	..	..	..	..	..	50		
7	Sol.-SS/Al	5.0	1	75	24	OK	34.3	0.7	35	10	11	52	12	..	..	..	..	..	..	..	..	..	..	50		
8	Sol.-SS/Al	0.2	2	75	24	OK	34.3	0.7	35	10	11	52	12	73	23	Clear	31.5	0.7	24	10	11	35	0.0148	12	Membranes wetted with CH <sub>2</sub> Cl <sub>2</sub> 0.0064 gm on bottom membrane.	
9	Sol.-SS/Al	0.2	2	75	24	OK	33.4	1.0	42	14	14	75	12	75	24	Clear	32.8	1.0	28	13	15	62	0.0222	11	0.0062 gm - bottom membrane.	
10	Sol.-SS/Al	0.2	2	73	23	OK	33.6	1.0	38	11	13	83	12	73	23	Clear	33.3	1.0	25	10	13	50	0.0020	11	0.0014 gm - bottom membrane.	
11	Sol.-SS/Al	0.2	1	66	19	OK	34.3	0.7	36	11	11	36	12	66	19	Clear	33.8	0.7	24	11	11	49	0.0362	9	0.8192 gm - bottom membrane. Total (50 cm <sup>3</sup> ).	
		1.0	1																					0.0003		
		3.0	1																						0.0012	
		5.0	1																						0.0002	
12	Sol.-SS/Al	0.2	1	67	19	OK	34.3	0.7	36	11	11	36	12	67	19	Clear	33.6	0.7	24	10	11	49	0.0062	9	0.0018 gm - Total (50 cm <sup>3</sup> ).	
		1.0	1																						0.0062	
		3.0	1																						-0.0018	
		5.0	1																						-0.0012	
		5.0	1																						0.0004	
13	Sol.-SS/Al	5.0	1	69	21	OK	34.2	0.7	36	11	11	36	12	69	21	Clear	31.8	0.8	28	11	12	48	0.0296	0.25	0.0148 gm - Total (50 cm <sup>3</sup> ).	
		3.0	1																						0.0296	
		1.0	1																						-0.0008	
		0.2	1																						0.0004	
		0.2	1																						0.0004	
14	Sol.-SS/Al	5.0	1	68	20	OK	34.7	0.7	41	12	12	41	12	68	20	Clear	33.6	0.7	27	12	12	46	0.0226	4	0.0118 gm - Membranes inseparable. Total (50 cm <sup>3</sup> ).	
		3.0	1																						0.0004	
		1.0	1																						0.0004	
		0.2	1																						0.0006	



definite decrease in the iron and aluminum contents of the acid upon filtration. Therefore, the values for the filtrate appear to be the solubility limits for iron and aluminum containing corrosion products in this particular acid at the temperature of the test. The fact that filtration caused no reduction in chromium or nickel content of the acid is interpreted to mean that the acid was not saturated with respect to salts of these elements. The clarity of the filtrate and the amounts of particulate matter isolated, substantiates the chemical analyses and reflects removal of particles of corrosion products. While it follows that the acid was saturated with metal salts of these particles, it does not follow that all of the salts of the same element had also reached their solubility limit. For example, the presence of particles of aluminum oxide, formed in the vapor phase, would prove that the solubility of aluminum oxide had been exceeded. The acid could also contain aluminum fluoride, at a level below its solubility product. The value of the latter would, of course, be reduced by the common use effect. These qualifications will be considered in more detail in Part III, Technical Discussion. The membranes were weighed separately before use, and post test, after drying overnight in a desiccator, at room temperature. The weight of particulate matter was doubled for reporting data in the conventional units of  $\text{gm}/100\text{ cm}^3$  (grams/100 cubic centimeters). Most of the particulate matter was retained on the top membrane, further certifying satisfactory filtration.

Tests 9 and 10 were made under the same conditions as Test 8, with another aliquot of acid from the same source. Similar trends were noted, but the variation in the aluminum contents of the filtrates strongly suggests that the acid contained different species, with different solubility limits. The results for chromium and nickel analyses were within the accuracy of the method. The wide variations in particulate matter weakened any argument for using this parameter as a simple measure of acid quality.

Tests 11 and 12 were performed with four filter membranes, arranged in the order of increasing pore size. As would be expected, the largest amount of particulate matter was found on the membrane, which had the smallest pore size. A negative value for the weight of particulate matter on any underlying membrane indicated that more material was leached from the membrane than was deposited thereon. This is to be expected because the membranes, though made of Teflon, have a hydrocarbon re-enforcement, and the weight changes for the membranes within the stack are small, approximately one milligram ( $\sim 1\text{ mg}$ ), approaching the accuracy of the method. In other cases, single bracketed values represent the combined weights of particulate matter of membranes held firmly together by the gelatinous nature of the material between them. The results from atomic absorption analyses of the filtrates fell within the range of the previous tests.

Tests 13 and 14 were performed with the membranes in the intended order, i.e., with the largest pore size on top. A relatively large loss in nitrogen oxide during filtration for Test 13 coincided with a low flow rate. This may be attributed to improper pretreatment with methylene chloride. Test 14 was normal in all respects. Post test analyses and determination of particulate matter gave equivalent results for both tests, indicating the insensitivity of the solubility of typical corrosion products to minor changes in nitrogen dioxide content or flow rate.

From these tests it was concluded that at least some of the particles removed from acid during filtration are gelatinous, and most of the particles are removed by the first membrane encountered. The arrangement of the membranes by pore size is not critical. The planned arrangement was used for subsequent tests because it was logical to place the membranes in the order of decreasing pore size.

It was also apparent from these tests that the application of nitrogen pressure should be discontinued as soon as possible, to avoid purging nitrogen dioxide from the filter. Pressurization was

stopped during the foregoing room temperature tests when flow of liquid was no longer observed. Direct, visual observation was not possible for low temperature tests because the equipment was placed inside a cold box. Attachment of a length of tubing between the vent of the flask in the cold box and a bubbler outside allowed discontinuation of pressurization before nitrogen dioxide was swept from the filtrate.

The acids for the Modified HDA tests first undertaken were blends reserved from long term storage of Modified HDA in small aluminum alloy and stainless steel tanks (Reference 2<sup>a</sup>). The tanks had been in storage for three years and contained relatively high concentrations of corrosion products. Blending was in a manner such as to give three stock solutions; one containing equivalent amounts of stainless steel and aluminum corrosion products, another containing an excess of aluminum corrosion products, and the third containing acid with an excess of stainless steel corrosion products. Nitrogen dioxide was added to one portion of each blend to bring the level from approximately 41 to 46 wt%. Water was added to another portion of each blend to raise the level from approximately 0.3 to 0.9 wt%. The solutions were stored several days after the additions to allow corrosion products to dissolve or precipitate, depending on their solubility at the new concentrations of nitrogen dioxide and water. Subsequently, a 50 cm<sup>3</sup> aliquot of each solution was filtered at room temperature. The data obtained are shown on page 1 of Table 19. This table has the same format as Table 18, and the same explanations apply.

Part of each blend tested at room temperature was stored in a cold box to allow changes in solubility at a lower temperature to be effected. Subsequently, a 50 cm<sup>3</sup> aliquot of each solution was filtered, with the equipment precooled to the same temperature in the cold box. Data gathered in support of these tests are shown on page 2 of Table 19.

Three questionable points were raised by the data from the room temperature tests. Atomic absorption analyses showed agreement in the composition of the filtrates for tests 1 and 2, but a larger amount of particulate matter was collected in the latter test, suggesting an error in analysis. A relatively large amount of particulate matter was found on the bottom membrane from several tests, suggesting contamination of the filtrate with particles, which would be hard to see in the highly colored (deep red) HDA solutions, but might affect subsequent atomic absorption analyses. A relatively high concentration for iron was found in the filtrate from test 7, compared with the filtrates from the other tests. Some of this could be attributed to attack on the filter assembly, some of the variation reflected the accuracy of the method. Three of the tests were repeated to resolve these discrepancies. The results are shown on page 3 of Table 19. The repeat of test 2 gave the same trends as noted originally, confirming earlier qualifications about reliability of particulate matter determinations. Test 5 was repeated with two, 0.2 $\mu$  membranes in the pack. No improvement in filtration efficiency or change in analytical results was found. A repeat of test 7 gave results similar to Tests 8 and 9. The difference in results between the original and repeat tests is attributed to the accuracy of the method. Variations in flow rates noted between the original and repeat tests are attributed to transfer of operations from an old laboratory to a new one with a slightly different pressurization system.

Based on analyses made in support of all the room temperature tests, it is concluded that the original blends were not saturated with stainless steel corrosion products. The blends were, however, saturated with one or more aluminum species. Addition of nitrogen dioxide or water did not change the results or conclusion drawn. The tendency toward higher flow rates and a somewhat larger loss of nitrogen dioxide during filtrations in the new facility are therefore incidental matters.

---

<sup>a</sup>Reference 2. "Long Term Storage of Modified HDA", H.Ph. Heubusch, Bell Aerospace Textron, AFRPL-TR-76-96, May 1977.

TABLE 19. CORROSION PRODUCT SOLUBILITY TESTS - SERIES 1 (1 of 4)

Test No.	Type HDA and CPs	Membranes		Acid Start										Filtrate										Flow Rate cm <sup>3</sup> /min	Comments	
		μ	No.	Temp.		Phys. Appear.	wt %			ppm (w/w)				N <sub>2</sub> Pres. psig	Temp.		Phys. Appear.	wt %			ppm (w/w)					
				°F	°C		NO <sub>2</sub>	H <sub>2</sub> O	Fe	Cr	Ni	Al	°F		°C	NO <sub>2</sub>		H <sub>2</sub> O	Fe	Cr	Ni	Al				
1	Mod. -SS/AI	5.0	1	72	22	P	42.7	0.3	8	2	3	8	11.5	72	22	Clear	41.6	0.3	7	2	3	5	0.0046	50 cm <sup>3</sup> Filtered.		
		3.0	1																				-0.0012	0.0016 gm Particulate.		
		1.0	1																				-0.0002			
		0.2	1																				0.0000			
2	Mod. +NO <sub>2</sub>	5.0	1	72	22	P	46.6	0.3	8	2	3	8	11.5	72	22	Clear	44.5	0.3	7	2	3	5	0.0020	Particulate.		
	-SS/AI	3.0	1																				0.0036			
		1.0	1																				0.0000			
		0.2	1																				-0.0002			
3	Mod. +H <sub>2</sub> O	5.0	1	72	22	P	42.3	0.9	8	2	3	9	11.5	72	22	Clear	40.7	1.0	7	2	3	5	0.0014	0.0018 gm Particulate.		
	-SS/AI	3.0	1																				-0.0004			
		1.0	1																				0.0026			
		0.2	1																				0.0000			
4	Mod. -AI>SS	5.0	1	70	21	P	42.4	0.3	6	2	3	9	11.5	70	21	Clear	41.1	0.4	6	3	4	7	0.0018	0.0016 gm Particulate.		
		3.0	1																				0.0008			
		1.0	1																				0.0006			
		0.2	1																				0.0006			
5	Mod. +NO <sub>2</sub>	5.0	1	72	22	P	46.1	0.3	6	2	3	9	11.5	72	22	Clear	44.7	0.4	6	2	3	6	0.0054	0.0026 gm Particulate.		
	-AI>SS	3.0	1																				-0.0012			
		1.0	1																				0.0004			
		0.2	1																				0.0006			
6	Mod. +H <sub>2</sub> O	5.0	1	72	22	P	42.6	0.9	6	2	3	8	11.5	72	22	Clear	40.1	1.0	6	2	3	6	0.0056	0.0021 gm Particulate.		
	-AI>SS	3.0	1																				-0.0020			
		1.0	1																				0.0000			
		0.2	1																				0.0006			
7	Mod. -SS>AI	5.0	1	72	22	P	42.7	0.3	11	2	3	6	11.5	72	22	Clear	41.5	0.3	12	2	3	4	0.0078	0.0027 gm Particulate.		
		3.0	1																				-0.0024			
		1.0	1																				0.0000			
		0.2	1																				0.0000			
8	Mod. +NO <sub>2</sub>	5.0	1	72	22	P	46.5	0.3	10	2	3	7	11.5	72	22	Clear	43.9	0.4	8	2	3	4	0.0056	0.0013 gm Particulate.		
	-SS>AI	3.0	1																				-0.0028			
		1.0	1																				-0.0002			
		0.2	1																				0.0000			
9	Mod. +H <sub>2</sub> O	5.0	1	72	22	P	42.5	0.8	13	2	3	7	11.5	72	22	Clear	41.0	0.8	9	2	3	5	0.0078	0.0037 gm Particulate.		
	-SS>AI	3.0	1																				-0.0016			
		1.0	1																				0.0004			
		0.2	1																				0.0008			



TABLE 19. CORROSION PRODUCT SOLUBILITY TESTS - SERIES I (3 of 4)

Test No.	Type MOA and CH	Membranes		Acid Start										Filtrate										Flow Rate cm <sup>3</sup> /min	Comments		
		μ	No.	Temp		Phys. Appearance	wt %		ppm (w/w)				N <sub>2</sub> Press psig	Temp °F	Phys. Appearance	wt %		ppm (w/w)				Particulate gm/100 cm <sup>3</sup>					
				°F	°C		NO <sub>2</sub>	H <sub>2</sub> O	Fe	Cu	Ni	Al				NO <sub>2</sub>	H <sub>2</sub> O	Fe	Cr	Ni	Al						
2	Mod. +NO <sub>2</sub> -SS/AI	5.0	1	72	22	P	46.6	0.3	8	2	3	8	11.5	72	22	Clear	44.5	0.3	7	2	3	5	0.0020	10	50 cm <sup>3</sup> Filtered. 0.0027 gm Particulate.		
		3.0	1																					0.0036			
		1.0	1																						0.0000		
		0.2	1																						0.0002		
2'	Mod. +NO <sub>2</sub> -SS/AI	5.0	1	72	22	P	47.2	0.3	8	2	3	8	11.5	70	21	Clear	44.9	0.3	6	3	5	8	0.0078	6	0.0037 gm Particulate.		
		3.0	1																						0.0012		
		1.0	1																						0.0002		
		0.2	1																						0.0006		
5	Mod. +NO <sub>2</sub> -AI>SS	0.5	1	72	22	P	46.1	0.3	6	2	3	9	11.5	72	22	Clear	44.7	0.4	6	2	3	5	0.0054	10	0.0526 gm Particulate.		
		3.0	1																						0.0012		
		1.0	1																						0.0004		
		0.2	1																						0.0006		
5'	Mod. +NO <sub>2</sub> -AI>SS	5.0	1	72	22	P	45.0	0.3	6	2	3	9	11.5	70	21	Clear	41.9	0.4	6	3	3	9	0.0044	25	0.0040 gm Particulate.		
		3.0	1																						0.0008		
		1.0	1																						0.0020		
		0.2	2																						0.0016		
																									0.0008		
7	Mod. SS>AI	5.0	1	72	22	P	42.7	0.3	11	2	3	6	11.5	72	22	Clear	41.5	0.3	12	2	3	4	0.0078	10	0.0027 gm Particulate.		
		3.0	1																						0.0024		
		1.0	1																						0.0000		
		0.2	1																						0.0000		
7'	Mod. SS>AI	5.0	1	72	22	P	42.7	0.3	13	2	3	9	11.5	72	22	Clear	39.3	0.4	10	4	6	1	0.0092	17	0.0051 gm Particulate.		
		3.0	1																						0.0002		
		1.0	1																						0.0002		
		0.2	1																						0.0008		

TABLE 19. CORROSION PRODUCT SOLUBILITY TESTS - SERIES 1 (4 of 4)

Test No.	Type HDA and CPs	Membranes		Acid-Start										r-Base										Particulate, gm/100 cm <sup>3</sup>	Flow Rate cm <sup>3</sup> /min	Comments
				Temp.		Phys. Appear.	wt %		ppm (w/w)				N <sub>2</sub> Press. psig	Temp.		Phys. Appear.	wt %		ppm (w/w)							
		μ	No.																				°F			
12	Med. +H <sub>2</sub> O -SS/AI	5.0	1	40	4	P	42.3	0.9	10	2	4	10	11.5	40	4	Clear	48.9	0.8	7	2	6	5	0.0020 0.0034 0.0014 0.0016	7	50 cm <sup>3</sup> Filtered. 0.0042 gm Particulate.	
12'	Med. +H <sub>2</sub> O -SS/AI	0.2	1	40	4	P	42.0	1.0	10	3	5	10	11.5	42	5	Clear	41.1	1.1	5	3	5	8	0.0040 -0.0005 0.0012 0.0005 0.0005	12	0.0039 gm Particulate.	
14	Med. +H <sub>2</sub> O -AI>SS	5.0	1	40	4	P	46.1	0.3	7	2	4	11	11.5	40	4	Clear	44.6	0.4	7	2	1	7	0.0032 -0.0016 0.0012 0.0002	10	0.0015 gm Particulate.	
14'	Med. +H <sub>2</sub> O -AI>SS	5.0	1	40	4	P	46.0	0.3	7	2	5	11	11.5	40	4	Clear	43.3	0.3	5	3	5	9	0.0030 0.0004 0.0006 0.0006 0.0006	5	0.0028 gm Particulate.	
18	Med. +H <sub>2</sub> O -SS>AI	5.0	1	40	4	P	42.6	0.8	15	2	4	11	11.5	40	4	Clear	41.2	0.8	13	2	4	5	0.0065 -0.0014 0.0004 0.0004	7	0.0030 gm Particulate.	
18'	Med. +H <sub>2</sub> O -SS>AI	5.0	1	40	4	P	42.0	0.9	15	3	4	11	11.5	42	5	Clear	38.7	0.7	8	4	6	7	0.0074 -0.0004 0.0002 0.0002 0.0002	12	0.0038 gm Particulate.	

Results from the tests performed with the same stock solutions filtered at 40°F (4°C) are given on page 3 of Table 19. As was to be expected, nitrogen dioxide losses were reduced by filtration at a lower temperature. Three tests were repeated and confirmed that apparent anomalies in the results for iron and nickel contents by atomic absorption analyses were merely a reflection of the accuracy of the method, and that particulate matter did not enter the filtrate. The results from these tests are given on page 4 of Table 19. A second, 0.2 $\mu$  membrane was included for each filtration. No real difference was found in the solubility of the corrosion products by reducing the temperature of the stock solutions from room temperature to 40°F (4°C). With the exception of one or more relatively insoluble species of aluminum, the solutions were not saturated. Graphing the data was therefore waived.

A second series of tests was conducted with other stock solutions containing higher concentrations of stainless steel corrosion products formed by contact of two different alloys with Standard and Modified HDA. The results from these tests are given in Table 20. It contains data gathered at room temperature by standard procedures, and tabulated in the same format as Tables 18 and 19, and data from tests with portions of each stock solution filtered at 40°F (4°C).

Test 1 involved a sample of Standard HDA retained from a corrosion test with 17-4 PH H-1025 stainless steel (Reference 1). Pre-analysis disclosed that the water content of the acid increased during storage. Post filtration analyses proved that the acid tested was saturated with one or more species of iron and chromium. Tests 2-4 involved portions of Modified HDA contaminated by corrosion of 304 stainless steel (Reference 1). Nitrogen dioxide or water were added to portions of this solution to match the levels reported in Table 19. Chemical analyses in support of test 2, with the 304 SS/Modified HDA stock solution, showed the latter to be unsaturated. This extended the solubility limits for iron, chromium and nickel above those reported in Table 19. No change in the solubility pattern was observed, within the accuracy of the analysis, for additions of nitrogen dioxide or water. The differences noted between Test 1 and 4 are attributed to differences in the corrosion inhibitor employed (and therefore different corrosion product species) and/or different water contents between the two acids tested. Too little data are available to interpret the effect of reduced nitrogen dioxide (Table 18) on the solubility of stainless steel corrosion products in Standard HDA.

Chemical analyses reported on the bottom of Table 20 proved that the solubility of corrosion products in the stock solutions tested did not change when the temperature was reduced to 40°F (4°C). Page 2 contains an additional test (No. 6) performed to further evaluate the effect of applied nitrogen pressure, and the resulting acid flow rate, on the composition of the filtrate. Test 5 was conducted using the standard level of nitrogen pressurization, 11.5 psia, and resulted in an acid flow rate of 25 cm<sup>3</sup>/min (cubic centimeters/minute). Nitrogen pressure was reduced to 5 psia for Test 6, with a corresponding reduction in flow rate to 10 cm<sup>3</sup>/min. The composition of the filtrates agreed within experimental error. Accordingly, flow rate was ruled out as an important variable in the test procedure.

A third series of tests was conducted with a blend of stock solutions formed by reactions between Modified HDA and 6061 aluminum alloy and 17-4 PH H-1025 stainless steel. The results of these tests are given in Table 21. Standardized methods were used to obtain the data, which are reported in the same manner as used for Tables 18-20.

Test 1 was conducted at room temperature. Because results for iron content, before and after filtration, fell within the accuracy of the method, no deduction about solubility limits for this metal is warranted. It is clear, however, that the stock solution was not saturated with salts of chromium, nickel or aluminum. Reducing the temperature of the same stock solution to 40°F

TABLE 20 CORROSION PRODUCT SOLUBILITY TESTS - SERIES 2

Test No.	Type HGA and CPs	Membranes		Acid Start										N <sub>2</sub> Press		Filtrate										Flow Rate cm <sup>3</sup> /min	Comments
				Temp		Phys. Appear.	wt %			ppm (wt/wt)						Temp.	Phys. Appear.	wt %			ppm (wt/wt)						
		μ	No	F	C		NO <sub>2</sub>	H <sub>2</sub> O	Fe	Cr	Ni	Al	F	C		NO <sub>2</sub>	H <sub>2</sub> O	Fe	Cr	Ni	Al						
1	Std.-SS -17.4 PH H-1825	5.0	1	72	22	P	43.8	1.7	98	34	36	<1	11.5	73	23	Clear	42.2	1.6	20	25	34	<1	0.0036	25	High Water Content. 50 cm <sup>3</sup> Filtered. 0.0330 gm Particulate.		
		3.0	1																								
		1.0	1																								
		0.2	1																								
2	Std.-SS -304	5.0	1	72	22	P	42.8	0.5	22	6	5	4	11.5	73	23	Clear	38.3	0.4	21	6	5	4	0.0010	25	0.0006 gm Particulate.		
		3.0	1																								
		1.0	1																								
		0.2	1																								
3	Std.-SS -304	5.0	1	72	22	P	46.7	0.5	21	6	5	4	11.5	73	23	Clear	43.8	0.4	19	6	4	4	0.0014	25	0.0014 gm Particulate.		
		3.0	1																								
		1.0	1																								
		0.2	1																								
4	Std.-SS -304	5.0	1	72	22	P	42.9	1.0	21	6	5	4	11.5	73	23	Clear	48.1	0.9	19	6	4	4	0.0014	25	0.0012 gm Particulate.		
		3.0	1																								
		1.0	1																								
		0.2	1																								
5	Std.-SS -17.4 PH H-1825	5.0	1	48	4	P	43.8	1.7	98	34	36	<1	11.5	42	5	Clear	41.5	1.7	19	26	37	<1	0.0008	25	High Water Content. 50 cm <sup>3</sup> Filtered. 0.0138 gm Particulate.		
		3.0	1																								
		1.0	1																								
		0.2	1																								
6	Std.-SS -17.4 PH H-1825	5.0	1	42	5	P	43.0	1.7	98	34	36	<1	8.8	43	6	Clear	41.3	1.6	20	28	34	<1	0.0576	10	Lower Flow Rate. 0.0239 gm Particulate.		
		3.0	1																								
		1.0	1																								
		0.2	1																								
7	Std.-SS -304	5.0	1	40	4	P	42.9	0.5	22	4	5	4	11.5	42		Clear	41.0	0.7	20	4	4	4	0.0004	25	0.0010 gm Particulate.		
		3.0	1																								
		1.0	1																								
		0.2	1																								
8	Std.-SS -304	5.0	1	40	4	P	46.7	0.5	22	4	5	4	11.5	42		Clear	45.6	0.5	19	4	4	4	0.0012	25	0.0014 gm Particulate.		
		3.0	1																								
		1.0	1																								
		0.2	1																								
9	Std.-SS -304	5.0	1	40	4	P	42.8	1.0	22	4	5	4	11.5	42		Clear	40.6	0.9	20	4	4	4	0.0008	25	0.0013 gm Particulate.		
		3.0	1																								
		1.0	1																								
		0.2	1																								



TABLE 21 CORROSION PRODUCT SOLUBILITY TESTS - SERIES 3

Test No	Type HDA and CH	Membranes		Acid Start										Filtrate										Flow Rate cm <sup>3</sup> min	Particulates gm 100 cm <sup>3</sup>	Comments																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																		
				Temp		Phys. Appear	wt %		ppm (w/w)						N <sub>2</sub> Press psig	Temp		Phys. Appear	wt %		ppm (w/w)																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
		μ	No.	°F	°C		NO <sub>2</sub>	H <sub>2</sub> O	Fe	Cr	Ni	Al	°F	°C		NO <sub>2</sub>	H <sub>2</sub> O		Fe	Cr	Ni	Al																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																						

(4°C), as was done for Test 2, had no effect on the solubilities of the species present in the acid. When the stock solution was modified by addition of water for Test 3, however, the solubility of iron specie(s) was decreased. Aluminum remained in solution at a relatively high concentration.

Test 4 was included to explain abortive attempts to extend the test matrix to still higher aluminum levels, by filtration of a sample highly contaminated with aluminum, by long term storage in an aluminum sampler, which had been filled without prior pickling. The acid came in contact with a synthetic rubber stopper during the filtration procedure. Post test analysis showed an increase in the aluminum content of the filtrate, presumably from the stopper. Pure Modified HDA was contaminated by exposure to the same type of stopper for Test 4. Analysis of the filtrate showed the large increase in aluminum content expected. The origin was a relatively soluble aluminum salt of the type previously postulated to explain the results of tests with corrosion products.

Too little data are available to allow deductions concerning the solubility of aluminum corrosion products in Standard HDA at low nitrogen dioxide content (Table 18), compared with the solubility of aluminum corrosion products in Modified HDA at higher nitrogen dioxide content.

The net result of Tests 1-4 was to extend the known solubility range of aluminum corrosion products beyond that reported in Table 19. Aluminum test vessels have been filled with Modified HDA and are being stored at elevated temperature (90°F (32°C)) to generate corrosion products for studies at still higher levels of aluminum.

## 2.2 Passivation Tests

Tests were conducted under a separate contract (Reference 3<sup>a</sup>) to determine if couples of the aluminum and stainless steel alloys in the Agena oxidizer tank sump become passive to Standard HDA during exposure periods up to 48 hours. The area ratio of the metals was matched to that in the sump, Al:SS:: 4:1. A relatively small value in reciprocal inches ( $1.4 \text{ in}^{-1}$ ) was used for S/V ratio (Surface-of-metal to Volume-of-acid). The tests indicated protection of the aluminum by the stainless steel, which appeared to act as a sacrificial anode. There was a steady rise in stainless steel corrosion products in solution, as determined by atomic absorption analyses, as a function of time. Passivation had not occurred within the two day period studied.

The experiment was refined and expanded during this program. All the aluminum and stainless steel alloys and heat treatments represented in the sump were included in the experiments. The S/V ratio was increased to  $10 \text{ in}^{-1}$ , to match that in the sump. The test time was extended to 28 days. A full complement of tests was run with Modified HDA. This included four alloys of aluminum (AA) and stainless steel (SS) tested separately for 28 days, 16 couples of the most common type in the sump (6061-T4 AA/304 SS cloth), at time intervals from 15 minutes to 28 days, and two, less common couples, tested for 28 days. Seven, parallel tests were run with Standard HDA. All of the Standard HDA tests were with the most common couple, at time intervals from 30 minutes to 28 days.

As indicated in Section 2.1, above, three batches of pure HDA were prepared for use in the solubility tests and were certified by analyses. Preparation and analyses were by standard procedures. The analytical data obtained were shown in Table 17. Portions of the same acids were used for the passivation tests.

---

<sup>a</sup>Reference 3. "Standard HDA Gel Study," Bell Aerospace Textron, Letter Report No. 6:843, 19 November 1976.

Test specimens were made from strips of aluminum alloy with different heat treatments (6061-T4 and 6061-T6), 304 stainless steel cloth and 347 stainless steel screen. The stainless steel cloth and stainless steel screen were supplied by LMSC (Lockheed Missiles and Space Company). The composition of each alloy was certified by emission spectroscopic analysis. The heat treatment of the aluminum alloys was verified by tensile tests.

The procedures used for preparing specimens for test were based on those used at LMSC for preparing the oxidizer tank sump. The 6061-T4 aluminum alloy was precleaned through a series of steps which began with a vapor degrease above trichloroethylene. The specimens were then alkaline cleaned, using Oakite 61B. Exposure time was 10 minutes at 190-210 °F (87.8-98.9°C). The alkaline cleaner was removed by rinsing in tap water for two minutes. The specimens were given a flash etch with a blend of nitric acid (20-30 volume) and hydrofluoric acid (2-3 volume). The etching was continued until the samples were visibly bright and clean. The acid solution was removed by rinsing with demineralized water, following which the specimens were blown dry with nitrogen. Next, the specimens were deoxidized by room temperature exposure to Clepo 180K for 2-5 minutes. The Clepo was displaced with potable water, and this, in turn, was displaced with demineralized water. The specimens were then blown dry with nitrogen.

Final cleaning was in accordance with LMSC Specification LAC 3150-060000. This step involved ultrasonic cleaning for 15-20 minutes with Freon TF.

The clean specimens were sealed in a clean, plastic bag and set aside until ready for use. Final cleaning and packaging were performed in a laminar flow clean room.

The stainless steel specimens were purchased precleaned by LMSC. The specimens were also ultrasonically cleaned in accordance with LAC 3150-060000, at Bell, then sealed in a clean, plastic bag and set aside until ready for use. Cleaning and packaging were performed in the same laminar flow clean room.

The 6061-T6 specimens, representing the cover for the sump, were also cleaned in accordance with instructions from LMSC. The first step consisted of degreasing the specimens with a methyl ethyl ketone wipe. This was followed by chemical cleaning, using Gee Bee R-66-C solution, at room temperature. Exposure time was 10 minutes. The cleaner contains orthophosphoric acid and hydrofluoric acid and was removed by a 10 minute rinse with deionized water. The specimens were dried with clean, hot (230°F (110°C)) air for 30 minutes.

The appearance of the test specimens is shown in Figure 18. The aluminum alloy had been cut into strips 1 inch wide and 24 inches long, pleated, and slotted to accept a stainless steel component. The stainless steel component consisted of a rectangular piece of cloth, approximately 1 inch wide and 2 inches long, or screen, approximately 1 inch wide and 14 inches long. The cleaning procedures previously described were employed with the separate test specimens in the form shown. Couples were formed by forcing the stainless steel components into the slots in the aluminum. The separate pieces were tared before assembly. The couples were weighed after final cleaning, as an assembly. Again, Agena oxidizer tank sump procedures were followed. The couples were ultrasonically cleaned for 5 minutes in Freon TF, then flushed with Freon TF. The flush fluid was subjected to particle count measurements according to LMSC Specification LAC 3150-050000. These steps were performed in laminar flow clean benches.

A relatively large test vessel was required to accommodate the width of the specimens. Vessels previously used for corrosion tests were adapted to the purpose. Adaptation consisted of



Figure 18. Passivation Test Specimens

removing the specimen holder normally attached to the Teflon liner in an aluminum body. A sketch of the test vessel is shown in Figure 19. Each test vessel was cleaned with a nitric acid-hydrofluoric acid solution to remove traces of aluminum or stainless steel corrosion products. The vessels were then filled with a 30 volume nitric acid solution and allowed to stand 72 hours. When subsequent atomic absorption analysis for each vessel disclosed less than 1 ppm (w/w (weight/weight)) of iron, chromium, nickel and aluminum, the vessel was rinsed with distilled water, dried in air at 230°F (110°C), and submitted for test.

A strip of aluminum alloy, or a strip of stainless steel, or a couple of aluminum alloy and stainless steel was added to a clean test vessel, after recording the physical appearance of the metal. The specimen was covered with a volume of 100 cm<sup>3</sup> (6 in.<sup>3</sup>) of pre-analyzed acid and the test vessel was closed. The test vessel was then set aside at room temperature for the length of time required to fill part of the test matrix. For tests of long duration, (days) the entire test assembly, consisting of the aluminum body and Teflon liner, was used. The liners, alone, were used for tests of short duration (hours).

A total of 29 tests was performed, including a duplicate of Test No. 11. Table 22 is a Test Log, which indicates the materials tested in each acid, and the numbers used to identify: the test, the sample and the acid, the test duration, and the dates on which each test was started and stopped. A set of pertinent comments completes the Log. As previously indicated, couples of aluminum alloy and stainless steel were tested in the majority of cases. Most of the couples consisted of 6061-T4 AA and 304 SS Cloth. Base-line data were obtained by testing, separately, strips of aluminum alloy and stainless steel. These samples are designated as "blanks" in Table 22.

In each case, the total area in square inches (or square centimeters) of the aluminum alloy strip was 48 in<sup>2</sup> (309.6 cm<sup>2</sup>). The actual area of the stainless steel specimens was 12 in<sup>2</sup> (77.4 cm<sup>2</sup>). The actual area of the stainless steel specimens was based on measurements of the diameter and length of the wires making up each type of specimen. The volume of acid used was 100 cm<sup>3</sup> (6 in<sup>3</sup>). The corresponding S/V ratios were, accordingly, 8 in<sup>-1</sup> for the aluminum alloys and 2 in<sup>-1</sup> for the stainless steels, when tested separately. The S/V ratio for the couples was 10 in<sup>-1</sup>. These parameters are summarized in Table 23.

A record was kept of temperature during storage. Values of 70 ± 5°F (21 ± 3°C) were recorded.

At the end of a given test, the top was removed from the test vessel, and the acid was siphoned into a clean bottle and submitted for analysis. The specimens were removed and visually examined. Acid was removed by rinsing with methylene chloride, following which, the specimens were air dried and weighed. Couples were disassembled and each component was washed with distilled water, rinsed with acetone, air dried and weighed. Test No. 11, a couple of 6061-T4 AA/304 SS, was repeated because a strand of stainless steel cloth was displaced during disassembly of the couple, negating the accuracy of the post test weighings. The difference between pre test and post test weights was used to establish the amount of deposit, in mg, on (or weight change for) a given couple. The difference in initial weight and weight after washing was used to calculate the corrosion rate, in mg/cm<sup>2</sup>, (milligrams per square centimeter) for a "blank" or a component of a given couple.

Acid samples submitted after passivation tests had been completed were subjected to the same treatment described for acid samples from corrosion product solubility tests Section (2.1). Briefly, this consisted of noting physical appearance and measuring temperature, before filtering 50 cm<sup>3</sup>, with a stainless steel pressure assembly, containing a stack of four Teflon membranes, arranged in the order of decreasing pore size, from 5 to 0.2 microns. A pressure of 5 psig (0.3 atm) nitrogen was applied to expedite filtration. The filtrate was examined visually and its temperature

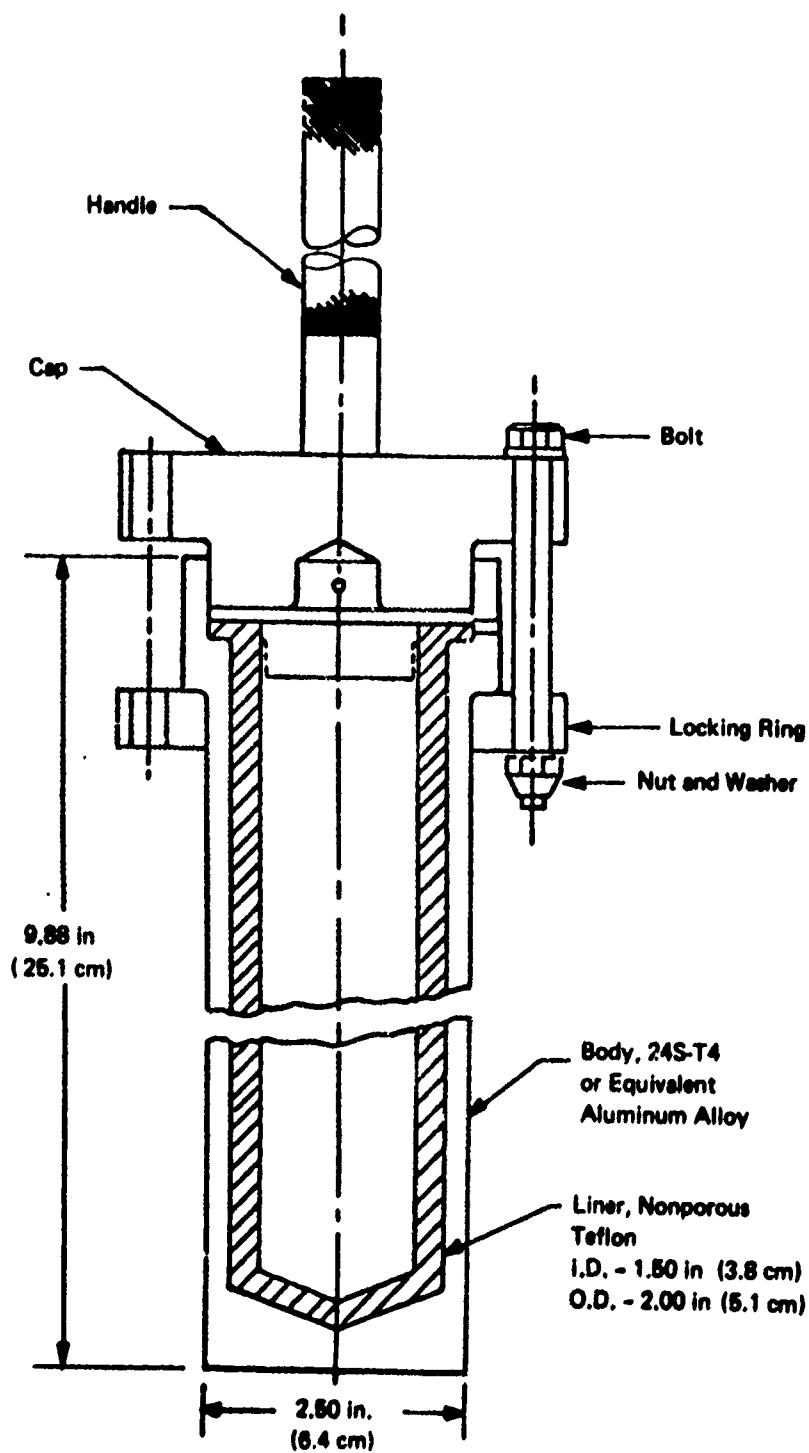


Figure 19. Passivation Test Vessel

TABLE 22. PASSIVATION TEST LOG

Test No.	Material(s)	Sample No.	Type HDA	Stock No.	Duration Days	Start	Stop	Comments
1	6061-T4 AA/304 SS Cloth	19	Modified	77-18	0 01	3-29-78	3-29-78	15 minutes.
2	6061-T4 AA/304 SS Cloth	18	Modified	77-18	0 02	3-29-78	3-29-78	30 minutes.
3	6061-T4 AA/304 SS Cloth	24	Standard	77-17	0 02	3-30-78	3-30-78	
4	6061-T4 AA/304 SS Cloth	17	Modified	77-18	0 04	3-20-78	3-20-78	1 hour.
5	6061-T4 AA/304 SS Cloth	23	Standard	77-17	0 04	3-20-78	3-20-78	
6	6061-T4 AA/304 SS Cloth	16	Modified	77-18	0 08	3-30-78	3-30-78	2 hours
7	6061-T4 AA/304 SS Cloth	15	Modified	77-18	0 17	3-31-78	3-31-78	4 hours.
8	6061-T4 AA/304 SS Cloth	14	Modified	77-18	0 33	3-29-78	3-29-78	8 hours.
9	6061-T4 AA/304 SS Cloth	13	Modified	77-18	0 67	3-29-78	3-29-78	16 hours
10	6061-T4 AA/304 SS Cloth	12	Modified	77-18	1	3-20-78	3-21-78	
11	6061-T4 AA/304 SS Cloth	22	Standard	77-17	1	3-20-78	3-21-78	
11R	6061-T4 AA/304 SS Cloth	29	Standard	77-17	1	4-25-78	4-26-78	Repeat Test
12	6061-T4 AA/304 SS Cloth	11	Modified	77-19	2	3- 6-78	3- 8-78	
13	6061-T4 AA/304 SS Cloth	21	Standard	77-17	2	3- 6-78	3- 8-78	
14	6061-T4 AA/304 SS Cloth	10	Modified	77-19	3	3- 6-78	3- 9-78	
15	6061-T4 AA/304 SS Cloth	9	Modified	77-19	4	3- 3-78	3- 7-78	
16	6061-T4 AA/304 SS Cloth	8	Modified	77-19	5	3- 2-78	3- 7-78	
17	6061-T4 AA/304 SS Cloth	7	Modified	77-19	7	2-21-78	2-28-78	
18	6061-T4 AA/304 SS Cloth	20	Standard	77-17	7	2-21-78	2-28-78	
19	6061-T4 AA/304 SS Cloth	6	Modified	77-19	14	2-21-78	3- 7-78	
20	6061-T4 AA/304 SS Cloth	5	Modified	77-19	21	2-23-78	3-16-78	
21	6061-T4 AA	2	Modified	77-19	28	2-14-78	3-14-78	Blank.
22	304 SS Cloth	26	Modified	77-19	28	2-15-78	3-15-78	Blank.
23	6061-T6 AA	25	Modified	77-19	28	2-15-78	3-15-78	Blank.
24	347 SS Screen	27	Modified	77-19	28	2-15-78	3-15-78	Blank.
25	6061-T4 AA/304 SS Cloth	1	Modified	77-19	28	2-14-78	3-14-78	
26	6061-T4 AA/304 SS Cloth	4	Standard	77-17	28	2-14-78	3-14-78	
27	6061-T6 AA/304 SS Cloth	28	Modified	77-19	28	2-27-78	3-27-78	
28	6061-T4 AA/347 SS Screen	3	Modified	77-19	28	2-14-78	3-14-78	

TABLE 23. PASSIVATION TEST PARAMETERS

Item	Surface Area cm <sup>2</sup>	Volume cm <sup>3</sup>
Aluminum Alloys	309.6	-
Stainless Steel Cloth	77.4	-
Stainless Steel Screen	77.4	-
Modified HDA	-	100.0
Standard HDA	-	100.0

was measured. Aliquots of the filtrate were then drawn and analyzed for nitrogen dioxide, water and metal content. Parallel analyses were made on the samples before filtration. The efficiency of the filtration process was judged in terms of the loss of nitrogen dioxide or gain in water contents. Differences in metal content for the solution as received and its filtrate provided an estimate of saturation with corrosion products. Comparison of the metal content of the filtrate with that of the stock solution (Table 17) indicated the degree of passivation which had been achieved. The membranes used during filtration were rinsed with methylene chloride to remove excess acid, dried overnight in a desiccator held at room temperature, and reweighed the following day. To the extent possible, the membranes were separated before the final weighing.

The results obtained for the metals subjected to passivation tests are shown in Tables 24 and 25, and Figures 20 - 22.

Table 24 contains principally, the results of weighings made in support of the passivation tests. The data are related to the Test Log by the Test No. Also shown are the material(s) tested, the type of HDA used, and the test duration. Tests 21 - 24 were the previously mentioned "blanks", i.e., tests in which a single metal rather than a couple was tested. This is also reflected in the columns of weights. Single, pre and post test weights appear for each "blank", in either the aluminum alloy or stainless steel column. The other weights shown in these columns are for the components of couples. Pre and post test weights of the couples complete the table.

Table 25 contains the results of post test inspections and calculations of the changes in weight and corrosion rates of the metals subjected to the passivation tests. Data are related to previous tables by Test No. The test run in duplicate is labeled, 11R. Also shown are the material(s) tested, the type of HDA used and the test duration. The materials include the "blanks" (Tests 21 - 24), and couples, as previously described. With one exception, there was no change in the appearance of the metal(s) through exposure to acid, for periods up to 28 days. This is signified by the symbol NE (No Effect) in the table. The exception involved a couple exposed to Standard HDA. The couple consisted of 6061-T4 AA/304 SS Cloth, the most prevalent combination in the Agena sump. Whereas the outer surface of the aluminum retained its metallic lustre, the crevice areas were dull in appearance, i.e., etched. The stainless steel remained dull gray. The weight changes reported for the metals were determined from the difference in the weight, in milligrams, of the specimen removed from test, rinsed free of acid and dried, and the weight of the specimen as put into the test. A positive value indicated formation of a film and/or a deposit of corrosion products. As noted under comments, no corrosion products were evident. A negative value indicated removal of a pre-existent film and/or corrosion. Values are considered accurate to  $\pm 0.2$  mg. The corrosion rates reported for the specimens were determined for the "blanks" and the separated parts of the couples, washed, dried and reweighed, after the test. The difference in weight, in milligrams, from start of the test to final weighing, divided by the area of the specimen, in square centimeters, is reported as corrosion rate. This designation is



TABLE 24. PASSIVATION TEST DATA

Test No.	Material(s)	Type HDA	Duration Days	Pre Test Weights -- gm			Post Test Weights -- gm		
				AA	SS	Couple	AA	SS	Couple
1	6061-T4 AA/304 SS Cloth	Modified	0.01	19.1202	4.4491	23.5683	19.1200	4.4495	23.5701
2	6061-T4 AA/304 SS Cloth	Modified	0.02	19.2600	3.8854	23.1449	19.2601	3.8859	23.1469
3	6061-T4 AA/304 SS Cloth	Standard	0.02	19.3802	4.4635	23.8485	19.3802	4.4689	23.8493
4	6061-T4 AA/304 SS Cloth	Modified	0.04	19.2650	3.9452	23.2104	19.2649	3.9461	23.2109
5	6061-T4 AA/304 SS Cloth	Standard	0.04	19.5992	4.3782	23.9782	19.5991	4.3791	23.9780
6	6061-T4 AA/304 SS Cloth	Modified	0.08	20.5962	4.0062	24.6016	20.5961	4.0068	24.6028
7	6061-T4 AA/304 SS Cloth	Modified	0.17	18.9655	4.2408	23.2058	18.9651	4.2420	23.2070
8	6061-T4 AA/304 SS Cloth	Modified	0.33	19.2267	4.1781	23.4053	19.2270	4.1794	23.4065
9	6061-T4 AA/304 SS Cloth	Modified	0.67	19.9708	3.8718	23.8428	19.9706	3.8729	23.8441
10	6061-T4 AA/304 SS Cloth	Modified	1	19.7382	3.8358	23.5740	19.7385	3.8357	23.5750
11	6061-T4 AA/304 SS Cloth	Standard	1	19.8697	4.2572	24.1270	19.8770	4.2331	24.1249
11R	6061-T4 AA/304 SS Cloth	Standard	1	19.6274	4.3105	23.9378	19.6254	4.3078	23.9353
12	6061-T4 AA/304 SS Cloth	Modified	2	20.6085	3.8658	24.4753	20.6382	3.8663	24.4754
13	6061-T4 AA/304 SS Cloth	Standard	2	19.4962	4.2761	23.7734	19.4951	4.2720	23.7686
14	6061-T4 AA/304 SS Cloth	Modified	3	19.2831	3.8843	23.1680	19.2830	3.8850	23.1684
15	6061-T4 AA/304 SS Cloth	Modified	4	20.5510	3.8790	24.4304	20.5519	3.8796	24.4317
16	6061-T4 AA/304 SS Cloth	Modified	5	20.1210	4.1900	24.3125	20.1221	4.1902	24.3126
17	6061-T4 AA/304 SS Cloth	Modified	7	19.2055	4.1931	23.4012	19.2060	4.1931	23.3992
18	6061-T4 AA/304 SS Cloth	Standard	7	20.8575	3.8812	24.7392	20.8578	3.8730	24.7308
19	6061-T4 AA/304 SS Cloth	Modified	4	18.0941	3.7895	21.8857	18.0949	3.7891	21.8845
20	6061-T4 AA/304 SS Cloth	Modified	21	19.8597	3.8561	23.7165	19.8600	3.8551	23.7155
21	6061-T4 AA	Modified	28	19.0500	.	.	19.0509	.	.
22	304 SS Cloth	Modified	28	.	4.1972	.	.	4.1958	.
23	6061-T6 AA	Modified	28	17.3253	.	.	17.3258	.	.
24	347 SS Screen	Modified	28	.	3.5609	.	.	3.5578	.
25	6061-T4 AA/304 SS Cloth	Modified	28	19.5508	4.6845	24.2360	19.5513	4.6831	24.2350
26	6061-T4 AA/304 SS Cloth	Standard	28	20.2070	4.0850	24.2920	20.2320	4.0721	24.3054
27	6061-T6 AA/304 SS Cloth	Modified	28	16.3737	4.0650	20.4377	16.3730	4.0630	20.4370
28	6061-T4 AA/347 SS Screen	Modified	28	21.5377	3.5048	25.0425	21.5388	3.5014	25.0406

TABLE 25. PASSIVATION TEST RESULTS - METALS

Test No.	Material(s)	Type HDA	Duration Days	Physical Appearance		Weight Change mg	CR - mg/cm <sup>2</sup>		Comments
				AA	SS		AA	SS	
1	6061-T4 AA/304 SS Cloth	Modified	0.01	NE	NE	1.8	-0.0006	0.0052	No CPs Noted.
2	6061-T4 AA/304 SS Cloth	Modified	0.02	NE	NE	2.0	0.0003	0.0065	No CPs Noted.
3	6061-T4 AA/304 SS Cloth	Standard	0.02	NE	NE	0.8	<0.0001	0.0052	No CPs Noted.
4	6061-T4 AA/304 SS Cloth	Modified	0.04	NE	NE	0.5	-0.0003	0.0116	No CPs Noted.
5	6061-T4 AA/304 SS Cloth	Standard	0.04	NE	NE	-0.2	-0.0003	0.0016	No CPs Noted.
6	6061-T4 AA/304 SS Cloth	Modified	0.08	NE	NE	1.2	-0.0003	0.0078	No CPs Noted.
7	6061-T4 AA/304 SS Cloth	Modified	0.17	NE	NE	1.2	-0.0013	0.0155	No CPs Noted.
8	6061-T4 AA/304 SS Cloth	Modified	0.33	NE	NE	1.2	0.0010	0.0168	No CPs Noted.
9	6061-T4 AA/304 SS Cloth	Modified	0.67	NE	NE	1.3	-0.0007	0.0142	No CPs Noted.
10	6061-T4 AA/304 SS Cloth	Modified	1	NE	NE	1.0	0.0010	-0.0013	No CPs Noted.
11	6061-T4 AA/304 SS Cloth	Standard	1	NE	NE	-2.1	0.0236	-0.3114	No CPs Noted.
11R	6061-T4 AA/304 SS Cloth	Standard	1	NE	NE	-2.5	-0.0065	-0.0349	No CPs Noted.
12	6061-T4 AA/304 SS Cloth	Modified	2	NE	NE	0.1	-0.0010	0.0065	No CPs Noted.
13	6061-T4 AA/304 SS Cloth	Standard	2	NE	NE	-4.8	-0.0036	-0.0530	No CPs Noted.
14	6061-T4 AA/304 SS Cloth	Modified	3	NE	NE	0.4	-0.0003	0.0091	No CPs Noted.
15	6061-T4 AA/304 SS Cloth	Modified	4	NE	NE	1.3	0.0029	0.0078	No CPs Noted.
16	6061-T4 AA/304 SS Cloth	Modified	5	NE	NE	0.1	0.0036	0.0026	No CPs Noted.
17	6061-T4 AA/304 SS Cloth	Modified	7	NE	NE	-2.0	0.0016	<0.0001	No CPs Noted.
18	6061-T4 AA/304 SS Cloth	Standard	7	NE	NE	-8.4	0.0010	-0.1060	No CPs Noted.
19	6061-T4 AA/304 SS Cloth	Modified	14	NE	NE	-1.2	0.0026	-0.0052	No CPs Noted.
20	6061-T4 AA/304 SS Cloth	Modified	21	NE	NE	-1.0	0.0010	-0.0129	No CPs Noted.
21	6061-T4 AA	Modified	28	NE	NE	0.9	0.0036	-	No CPs Noted.
22	304 SS Cloth	Modified	28	NE	NE	-1.4	-	-0.0181	No CPs Noted.
23	6061-T6 AA	Modified	28	NE	NE	0.5	0.0016	-	No CPs Noted.
24	347 SS Screen	Modified	28	NE	NE	-3.1	-	0.0413	No CPs Noted.
25	6061-T4 AA/304 SS Cloth	Modified	28	NE	NE	-1.0	0.0016	-0.0181	No CPs Noted.
26	6061-T4 AA/304 SS Cloth	Standard	28	Dull Areas Between Folds	NE	13.4	0.0807	-0.1667	No CPs Noted.
27	6061-T6 AA/304 SS Cloth	Modified	28	NE	NE	-0.7	-0.0023	-0.0258	No CPs Noted.
28	6061-T4 AA/304 SS Screen	Modified	28	NE	NE	-1.9	0.0036	-0.0439	No CPs Noted.

appropriate for negative values in the table. Positive values indicate film formation. Corrosion rates are considered accurate to  $\pm 0.0006 \text{ mg/cm}^2$ , for the aluminum alloys, and  $\pm 0.0025 \text{ mg/cm}^2$ , for the stainless steels.

Figure 20 is a plot of weight change, in milligrams, for the 6061-T4 AA/304 SS Cloth couples exposed to HDA, as a function of time. Page 1 contains data for tests from 0-24 hours in duration. Page 2 contains data for tests from 0-28 days in duration. Divisions for the ordinate were compressed from page 1 to encompass all the data for the longer term tests. Each page contains a smoothed curve for tests with Modified HDA, and a second curve for tests with Standard HDA. The curves were smoothed in line with the accuracy of the data, and the additive nature of the test. Less data points were available for the Standard HDA curve, therefore, less confidence is placed in its locus.

Figure 21 is a plot of the corrosion rate, in  $\text{mg/cm}^2$ , of 6061-T4 aluminum alloy exposed to HDA as a function of time. Page 1 contains smoothed data for the aluminum alloy coupled to 304 SS Cloth and exposed to Modified HDA or Standard HDA, for periods of 0-24 hours. Page 2 contains the corresponding curves for the aluminum alloy exposed, as a couple, for periods of 0-28 days. Again, divisions for the ordinate were compressed for page 2, to allow presentation of all the data. Shown for comparison is the corrosion rate of the aluminum alloy "blank" exposed to Modified HDA for 28 days.

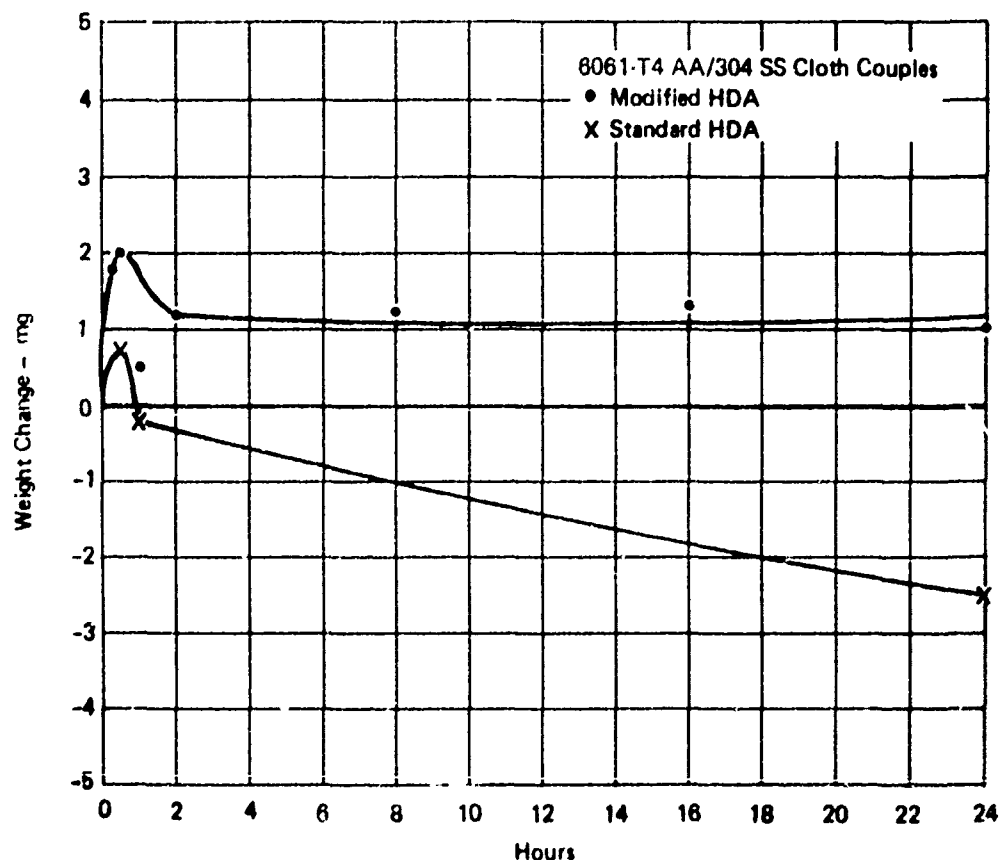


Figure 20. Passivation Test Results - Weight Change - Metals (1 of 2)

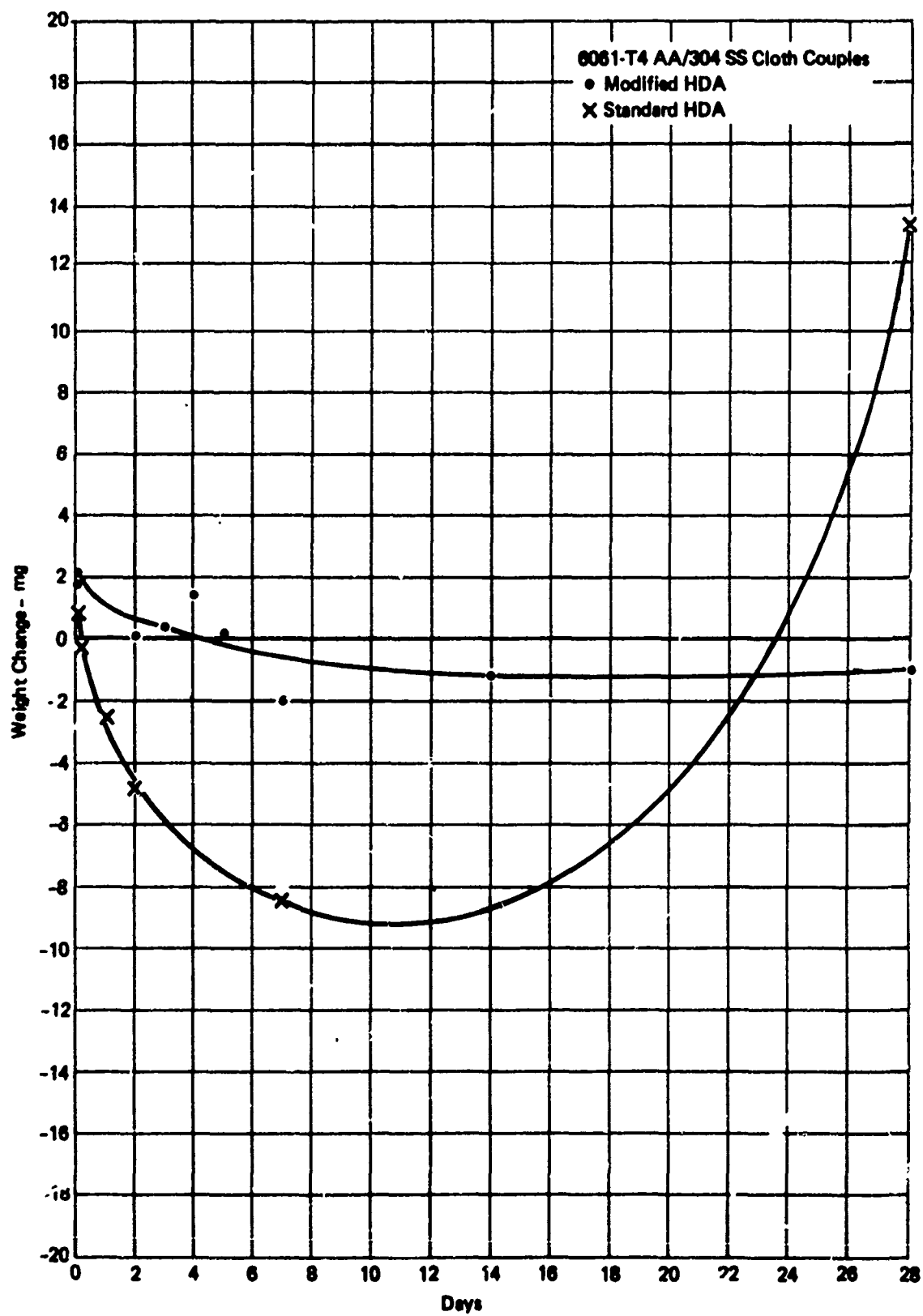


Figure 20. Passivation Test Results - Weight Change - Metals (2 of 2)

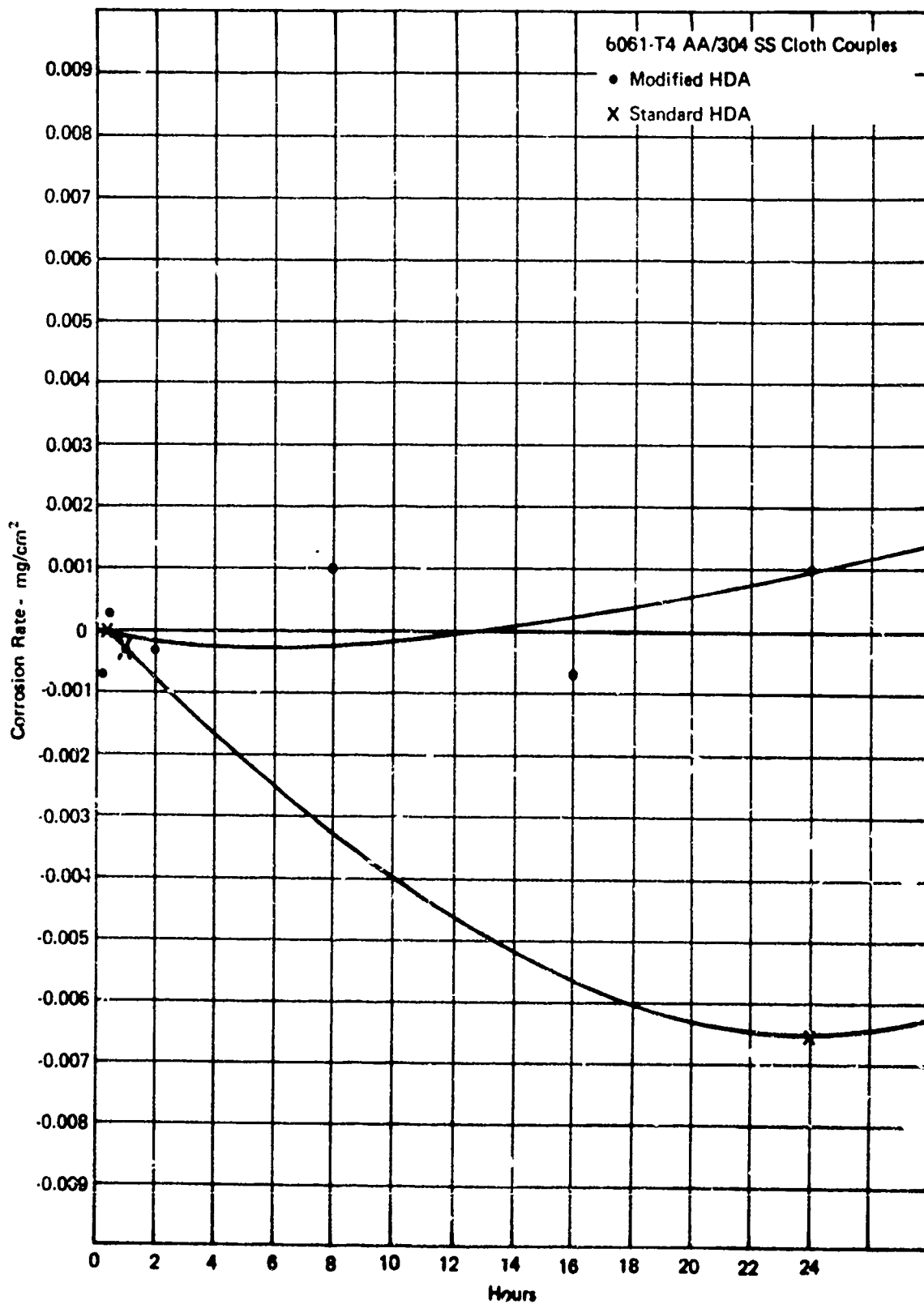


Figure 21. Passivation Test Results - Corrosion Rate - Aluminum Alloy (1 to 2)

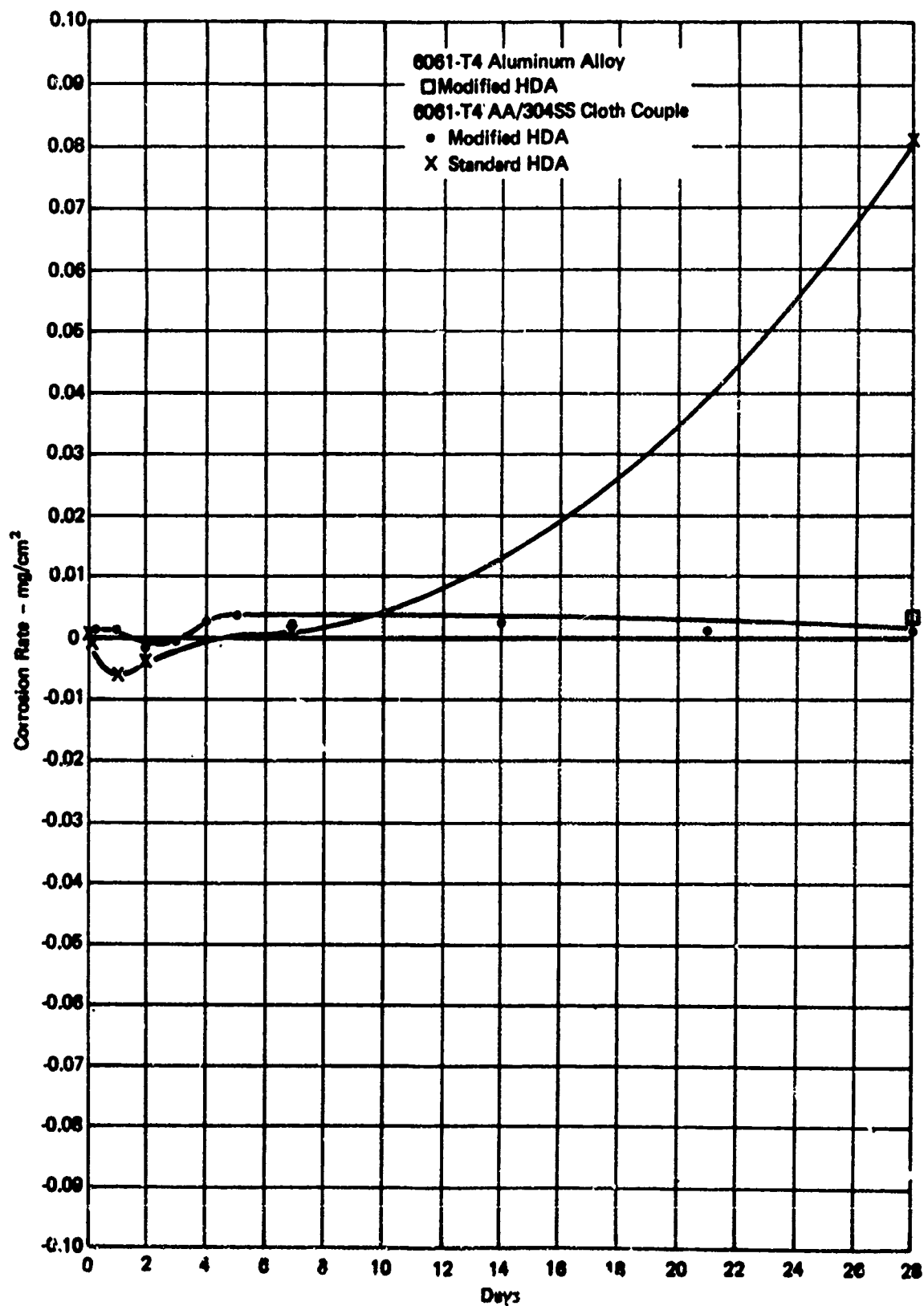


Figure 21. Passivation Test Results - Corrosion Rate - Aluminum Alloy (2 of 2)

Figure 22 is a plot of the corrosion rate, in  $\text{mg}/\text{cm}^2$ , as a function of time of the 304 stainless steel components of the couples for which the corrosion rate of the aluminum alloy components was plotted in Figure 21. The same conventions and qualifications apply to each component. Shown for comparisons on page 2 of Figure 22 is the corrosion rate of the stainless steel "blank" exposed to Modified HDA for 28 days.

The results obtained for the acids subjected to passivation tests are shown in Table 26 and Figures 23-26.

Table 26 is arranged by Test No. in order to allow easy comparison of results for the metals and acids tested together. Also shown are the type of HDA used for each test, the stock solution from which the acid was drawn, and its nitrogen dioxide content, as loaded into the passivation test vessel. Next is shown the time the metal and acid were left in contact. A set of chemical analyses of the acid removed from the passivation test vessel includes the appearance of the acid, its nitrogen dioxide and water contents, in weight percent, and the apparent, total amounts, in ppm, of iron chromium and nickel in the acid, from attack on stainless steel test specimens, and aluminum, from attack on an aluminum alloy test specimen. These are considered apparent, total amounts, because they represent analysis of a sample before filtration. In addition to soluble salts, such samples may contain particles of corrosion products for which accurate analyses are difficult, because of the difficulty of ensuring feed of a homogeneous aliquot of the sample to the flame of the atomic absorption spectrophotometer used for metal analyses. A second set of analyses represents the composition of the acid after filtration. Higher reliance is placed in the measured values for metals in the filtrate because more homogeneous solutions were aspirated into the flame of the atomic absorption spectrophotometer. The efficiency of the filtration procedure is indicated by the slight changes in temperature measured before and after filtration, the normal flow rates employed, and the constancy of water contents and relatively small changes in nitrogen dioxide contents found, before and after filtration. Values reported for metal contents were adjusted, as was done for corrosion product solubility tests, to account for attack on the pressure filter assembly. Occasional reports of a higher concentration for a given metal after filtration are explained by the previously stated (Section 2.1) accuracy of the method. Values for particulate matter collected during filtration are also reported as described for solubility tests. These data are considered unreliable because they follow no set pattern. A set of comments including the identity of the material(s) exposed to a given acid, the duration of short term tests in hours, the volume of acid filtered, and the total weight of particulate matter collected from the stated volume of acid completes the table. Values below the sensitivity of the balance ( $\pm 0.0001$  gm) were left unreported except for the comment that the data were not applicable (N/A), i.e., not reliable.

Test No. 11R was an exception to the explanation given above. This test was repeated to obtain more reliable data about the weight change of the couple exposed to acid. The acid was filtered post test, but supporting analyses were limited to those necessary to certify the validity of the test.

Figure 23 is a plot of the buildup of iron in solution as a function of time, as judged by analysis of filtrates from the passivation tests. Page 1 contains data for tests of 0-24 hours duration. Page 2 contains data for tests of 0-28 days duration. The letters A, B, C, will be discussed in Section III. The same divisions are used for the ordinate on both pages. Each page contains a curve, smoothed to reflect the accuracy of the method, and the nature of the test, for the points obtained from tests with Modified HDA, and a curve for the points obtained for the relatively few tests with Standard HDA. The point shown for Standard HDA at 24 hours (1 day) is from the more reliable repeat test, 11R. Although less points are available for standard HDA, and, therefore, the exact locus of this

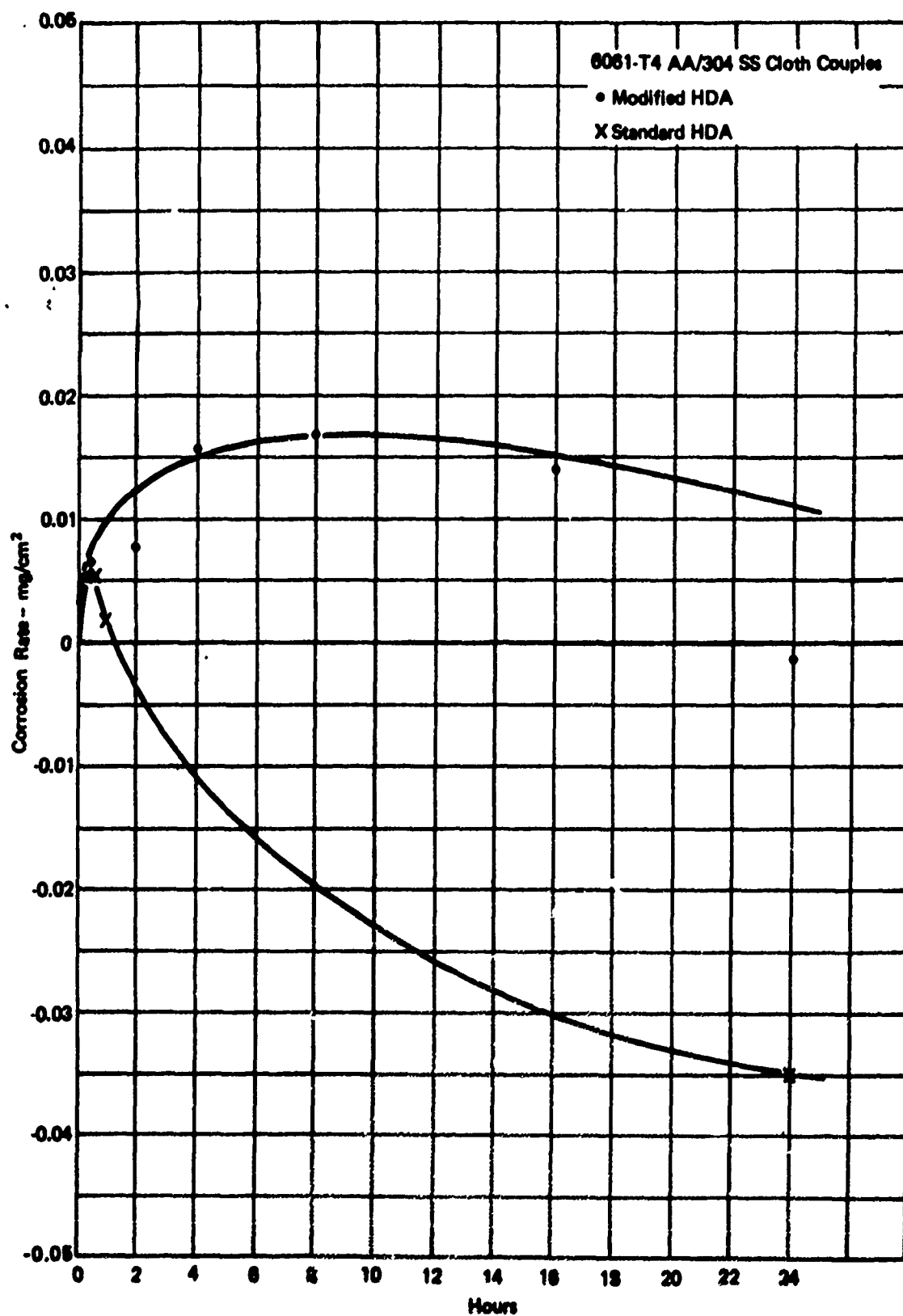


Figure 22. Passivation Test Results - Corrosion Rate - Stainless Steel (1 of 2)



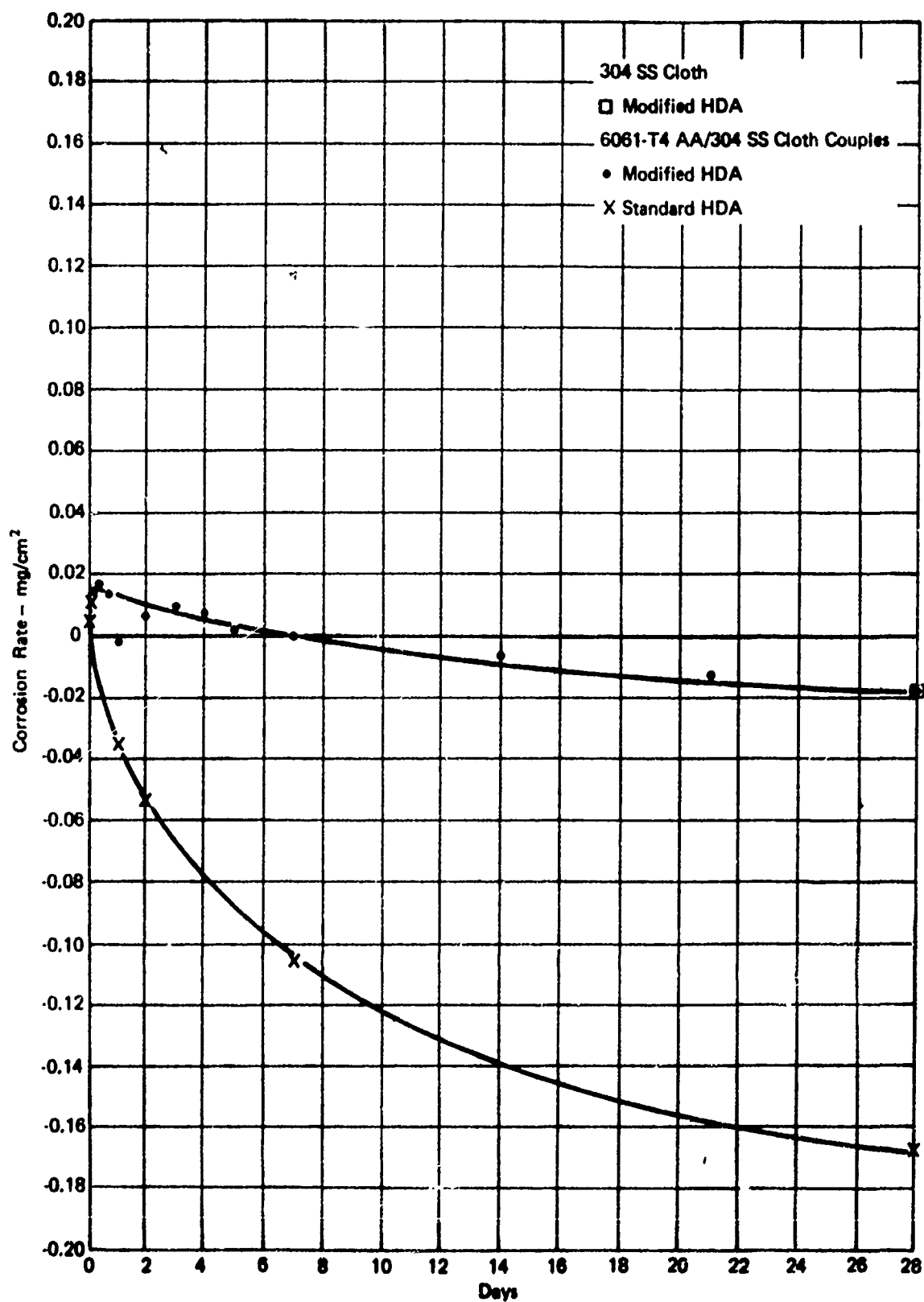


Figure 22. Passivation Test Results - Corrosion Rate - Stainless Steel (2 of 2)



TABLE 26. PASSIVATION TEST RESULTS - ACIDS (2 of 3)

Test No.	Type HDA (Stock No.)	wt % NO <sub>2</sub> Pts	Test Duration Days	Acid Before Filtration										Filtration										Comments	
				Temp.		Phys. Appear.	wt %		ppm (w/w)		Flow Rate cm <sup>3</sup> /min	Temp.		Phys. Appear.	wt %		ppm (w/w)		Particulate gm/100 cm <sup>3</sup>						
				°F	°C		NO <sub>2</sub>	H <sub>2</sub> O	Fe	Cr		Ni	A		°F	°C	NO <sub>2</sub>	H <sub>2</sub> O		Fe	Cr	Ni	Al		
11	Standard (77-7)	43.6	1	75.0	23.9	Clear	42.7	0.5	14	3	2	2	25	75.0	23.9	Clear	42.1	0.5	14	2	3	2	5.0	0.0006	6061-T4 AA/304 SS Cloth. 50 cm <sup>3</sup> Filtered.
																							3.0	-0.0012	-0.0003 gm Particulate.
																							1.0	0.0004	
																							0.2	-0.0003	
11R	Standard (77-17)	43.5	1	75.0	23.9	Clear	42.6	0.5	10	2	2	2	25	75.0	23.9	Clear			11				5.0	...	6061-T4 AA/304 SS Cloth. 50 cm <sup>3</sup> Filtered.
																							3.0	...	Partial Analysis Filtrate.
																							1.0	...	
																							0.2	...	
12	Modified (77-19)	43.4	2	75.0	23.9	Clear	43.3	0.4	2	<1	<1	<1	25	75.0	23.9	Clear	41.9	0.4	2	<1	<1	<1	5.0	-0.0004	6061-T4 AA/304 SS Cloth. 50 cm <sup>3</sup> Filtered.
																							3.0	...	0.0005 gm Particulate.
																							1.0	0.0010	
																							0.2	0.0004	
13	Standard (77-17)	43.7	2	75.0	23.9	Clear	42.1	0.4	15	4	3	<1	7	75.0	23.9	Clear	40.0	0.4	15	4	3	<1	5.0	0.0024	6061-T4 AA/304 SS Cloth. 50 cm <sup>3</sup> Filtered.
																							3.0	-0.0016	0.0008 gm Particulate.
																							1.0	0.0002	
																							0.2	0.0006	
14	Modified (77-19)	43.4	3	74.0	23.3	Clear	42.1	0.4	3	<1	<1	2	25	74.0	23.3	Clear	41.6	0.4	3	<1	<1	1	5.0	0.0012	6061-T4 AA/304 SS Cloth. 50 cm <sup>3</sup> Filtered.
																							3.0	-0.0008	0.0005 gm Particulate.
																							1.0	0.0004	
																							0.2	0.0002	
15	Modified (77-19)	43.4	4	74.0	23.3	Clear	42.6	0.4	3	<1	<1	2	25	74.0	23.3	Clear	40.3	0.4	3	<1	<1	2	5.0	0.0008	6061-T4 AA/304 SS Cloth. 50 cm <sup>3</sup> Filtered.
																							3.0	-0.0012	0.0000 gm Particulate.
																							1.0	0.0000	
																							0.2	-0.0004	
16	Modified (77-19)	43.4	5	74.0	23.3	Clear	42.2	0.4	4	<1	<1	2	25	74.0	23.3	Clear	41.5	0.4	4	<1	<1	1	5.0	0.0016	6061-T4 AA/304 SS Cloth. 50 cm <sup>3</sup> Filtered.
																							3.0	-0.0010	0.0012 gm Particulate.
																							1.0	0.0006	
																							0.2	0.0012	
17	Modified (77-19)	43.3	7	74.0	23.3	Clear	42.4	0.4	5	<1	1	2	25	74.0	23.3	Clear	41.3	0.4	5	<1	1	2	5.0	0.0022	6061-T4 AA/304 SS Cloth. 50 cm <sup>3</sup> Filtered.
																							3.0	...	0.0026 gm Particulate.
																							1.0	0.0018	
																							0.2	...	
18	Standard (77-17)	43.2	7	74.0	23.3	Clear	42.2	0.4	33	8	7	2	14	73.0	22.8	Clear	41.3	0.5	22	8	7	<1	5.0	0.0030	6061-T4 AA/304 SS Cloth. 50 cm <sup>3</sup> Filtered.
																							3.0	...	0.0026 gm Particulate.
																							1.0	0.0022	
																							0.2	...	
19	Modified (77-19)	43.3	14	74.0	23.3	Clear	42.3	0.4	7	1	1	2	25	74.0	23.3	Clear	41.2	0.4	7	1	1	2	5.0	0.0010	6061-T4 AA/304 SS Cloth. 50 cm <sup>3</sup> Filtered.
																							3.0	-0.0014	0.0004 gm Particulate.
																							1.0	0.0006	
																							0.2	0.0006	
20	Modified (77-19)	43.4	21	75.0	23.9	Clear	40.6	0.4	9	1	2	2	25	75.0	23.9	Clear	39.5	0.4	9	1	2	2	5.0	0.0006	6061-T4 AA/304 SS Cloth. 50 cm <sup>3</sup> Filtered.
																							3.0	0.0000	0.0005 gm Particulate.
																							1.0	0.0004	
																							0.2	0.0000	

TABLE 26. PASSIVATION TEST RESULTS - ACIDS (3 of 3)

Test No	Type HDA (Stock No.)	wt % NO <sub>2</sub> Frs	Test Duration Days	Acid Before Filtration										Filtrate										Particulate	Comments		
				Temp.		Phys. Appear.	wt %		ppm (wt/wt)				Flow Rate cm <sup>3</sup> /min		Temp.		Phys. Appear.	wt %		ppm (wt/wt)						μ Membr.	gm/100 cm <sup>3</sup>
				°F	°C		NO <sub>2</sub>	H <sub>2</sub> O	Fe	Cr	Ni	Al	°F	°C	NO <sub>2</sub>	H <sub>2</sub> O		Fe	Cr	Ni	Al						
21	Modified (77-19)	43.4	28	75.0	23.9	Clear	41.9	0.4	1	<1	<1	2	25	75.0	23.9	Clear	40.5	0.4	1	<1	<1	2	5.0 3.0 1.0 0.2	6061-T4 AA Blank. 50 cm <sup>3</sup> Filtered. -0.0005 gm Particulate.			
22	Modified (77-19)	43.3	28	75.0	23.9	Clear	42.1	0.4	12	2	2	3	25	75.0	23.9	Clear	40.7	0.4	12	2	2	2	5.0 3.0 1.0 0.2	304 SS Cloth Blank. 50 cm <sup>3</sup> Filtered. 0.0006 gm Particulate.			
23	Modified (77-19)	43.3	28	75.0	23.9	Clear	42.1	0.4	1	<1	<1	2	25	75.0	23.9	Clear	40.8	0.4	1	<1	<1	2	5.0 3.0 1.0 0.2	6061-T6 AA Blank. 50 cm <sup>3</sup> Filtered. 0.0002 gm Particulate.			
24	Modified (77-19)	43.3	28	75.0	23.9	Clear	41.8	0.4	9	1	2	<1	25	75.0	23.9	Clear	40.4	0.4	9	1	2	<1	5.0 3.0 1.0 0.2	347 SS Screen Blank. 50 cm <sup>3</sup> Filtered. -0.0001 gm Particulate.			
25	Modified (77-19)	43.4	28	75.0	23.9	Clear	40.7	0.4	10	2	2	2	25	75.0	23.9	Clear	38.4	0.4	11	2	2	2	5.0 3.0 1.0 0.2	6061-T4 AA/304 SS Cloth. 50 cm <sup>3</sup> Filtered. -0.0003 gm Particulate.			
26	Standard (77-17)	43.9	28	75.0	23.9	Cloudy	41.8	8.5	28	26	28	2	25	75.0	23.9	Clear	40.9	0.5	24	26	29	2	5.0 3.0 1.0 0.2	6061-T4 AA/304 SS Cloth. 50 cm <sup>3</sup> Filtered. 0.0008 gm Particulate.			
27	Modified (77-19)	43.2	28	75.0	23.9	Clear	41.7	0.4	10	2	2	2	25	75.0	23.9	Clear	39.5	0.4	12	2	2	2	5.0 3.0 1.0 0.2	6061-T6 AA/304 SS Cloth. 50 cm <sup>3</sup> Filtered. -0.0003 gm Particulate.			
28	Modified (77-19)	43.4	28	75.0	23.9	Clear	42.2	0.4	13	3	2	2	25	75.0	23.9	Clear	40.6	0.4	13	3	2	2	5.0 3.0 1.0 0.2	6061-T4 AA/347 SS Screen. 50 cm <sup>3</sup> Filtered. 0.0008 gm Particulate.			

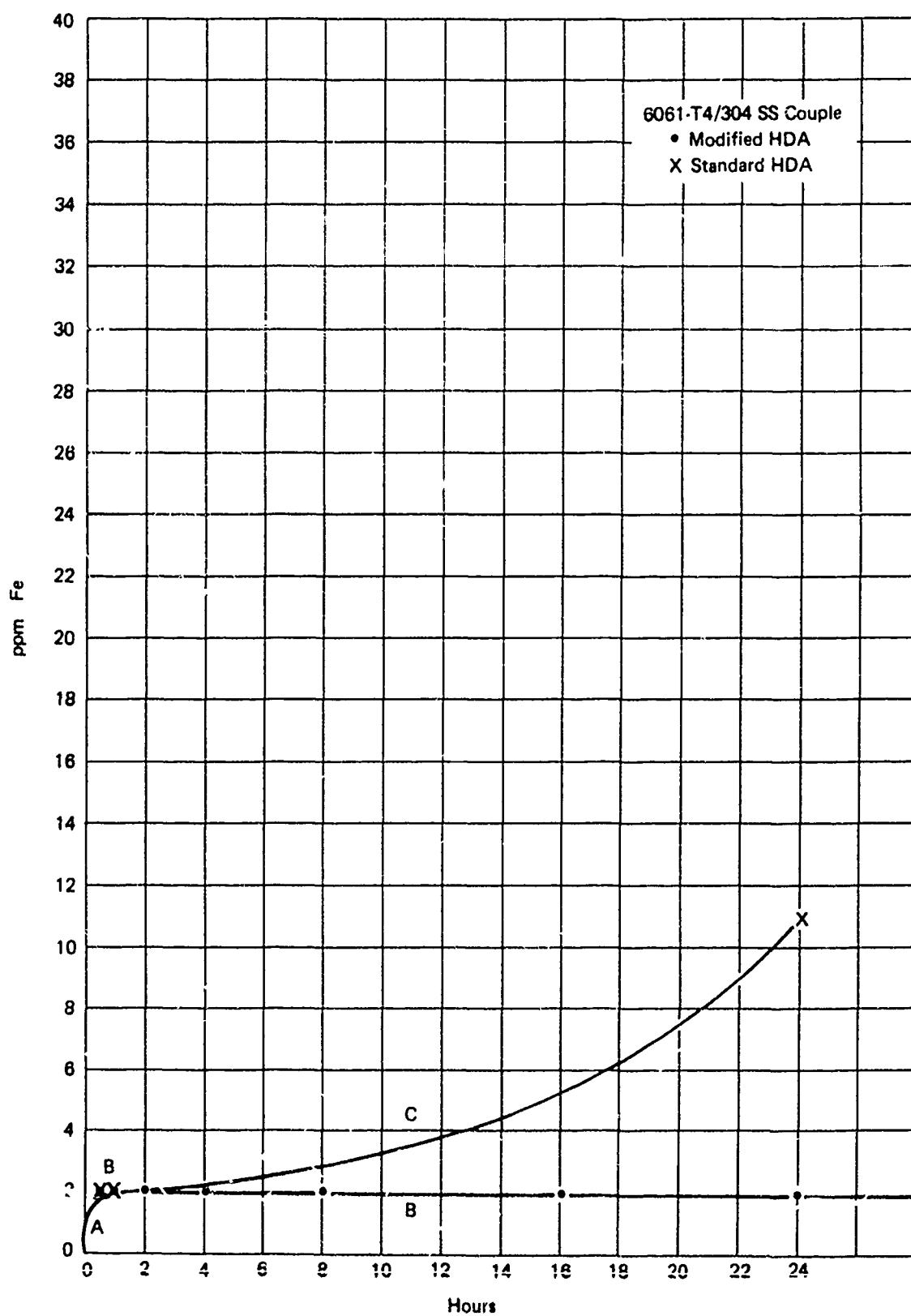


Figure 23. Passivation Tests - Iron Buildup In Solution (1 of 2)

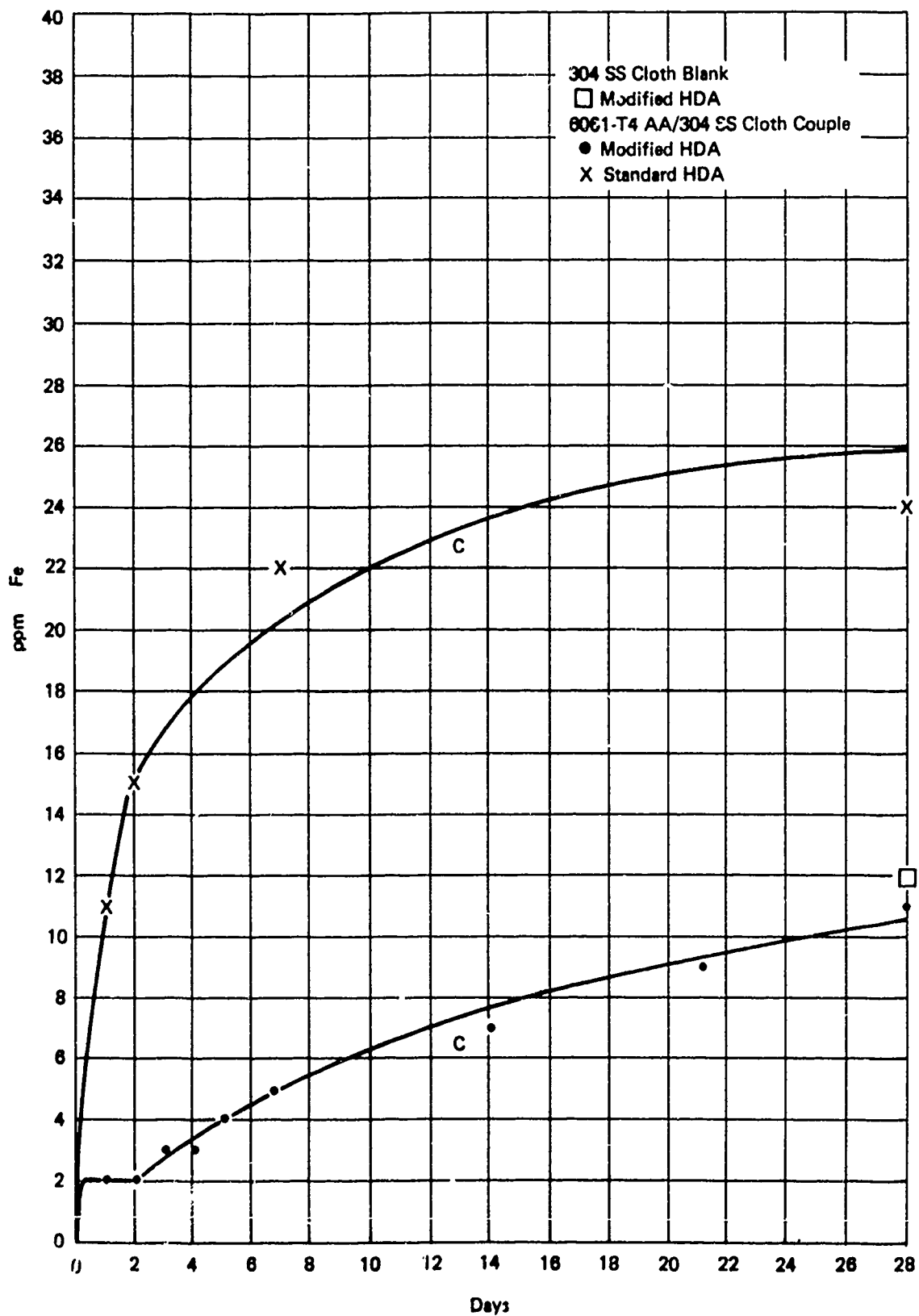


Figure 23. Passivation Tests - Iron Buildup In Solution (2 of 2)

curve is in doubt, there is no question about the fact that any given time, after the first hour, for which comparative data are available, Standard HDA is more corrosive than Modified HDA. One additional point plotted on page 2 represents corrosion of the 304 stainless steel "blank" exposed to Modified HDA for 28 days. No comparable data were obtained with Standard HDA.

Figure 24 is a plot of chromium buildup in solution during the passivation tests. The plot was constructed as explained for iron buildup. No data for the filtrate from the repeat test, 11R, were obtained because chromium concentration was so low at the time that its solubility could not have been exceeded. The value for the chromium content of the acid before filtration is therefore a reliable indication of chromium content at 24 hours (1 day). The point is proven by the fact that the chromium content measured before filtration for the repeat test agreed within experimental error with the values before and after filtration for test, No. 11. At all times for which comparable data were obtained, Standard HDA was more corrosive to 304 stainless steel than was Modified HDA. Within 28 days, the concentration of chromium in Standard HDA had exceeded the concentration of iron. At 28 days the chromium content from the "blank" in Modified HDA matched that of the corresponding couple in the same acid.

Figure 25 is a plot of nickel buildup in solution during the passivation tests. The plot was constructed as explained above. The same explanation given for chromium content for repeat test, 11R, applies to nickel. Also, as was the case with chromium, the data for nickel prove that Standard HDA was more corrosive toward 304 stainless steel than was Modified HDA. Within 28 days, the concentration of nickel in Standard HDA had exceeded that of iron and chromium. At 28 days, the concentration of nickel in Modified HDA was at the same level from exposure to the 304 stainless steel "blank" as from exposure of the acid to a 6061-T4 AA/304 SS couple.

Figure 26 is a plot of aluminum buildup in solution during the passivation tests. The plot was constructed as explained above. The same explanation given for chromium and nickel contents for repeat test, 11R, applies to aluminum. Neither acid was very corrosive to aluminum. Differences in aluminum content, plotted as functions of time and type of acid used, are within the limits of the method of analysis. Results for repeat test, 11R, are equivalent to those shown for Test No. 11. Results at 28 days for the "blank" tested in Modified HDA and couples, tested in Modified HDA and Standard HDA, are likewise equivalent.

Further deductions from the chemical analyses will be found in the Technical Discussion, which follows as Section III of this report.

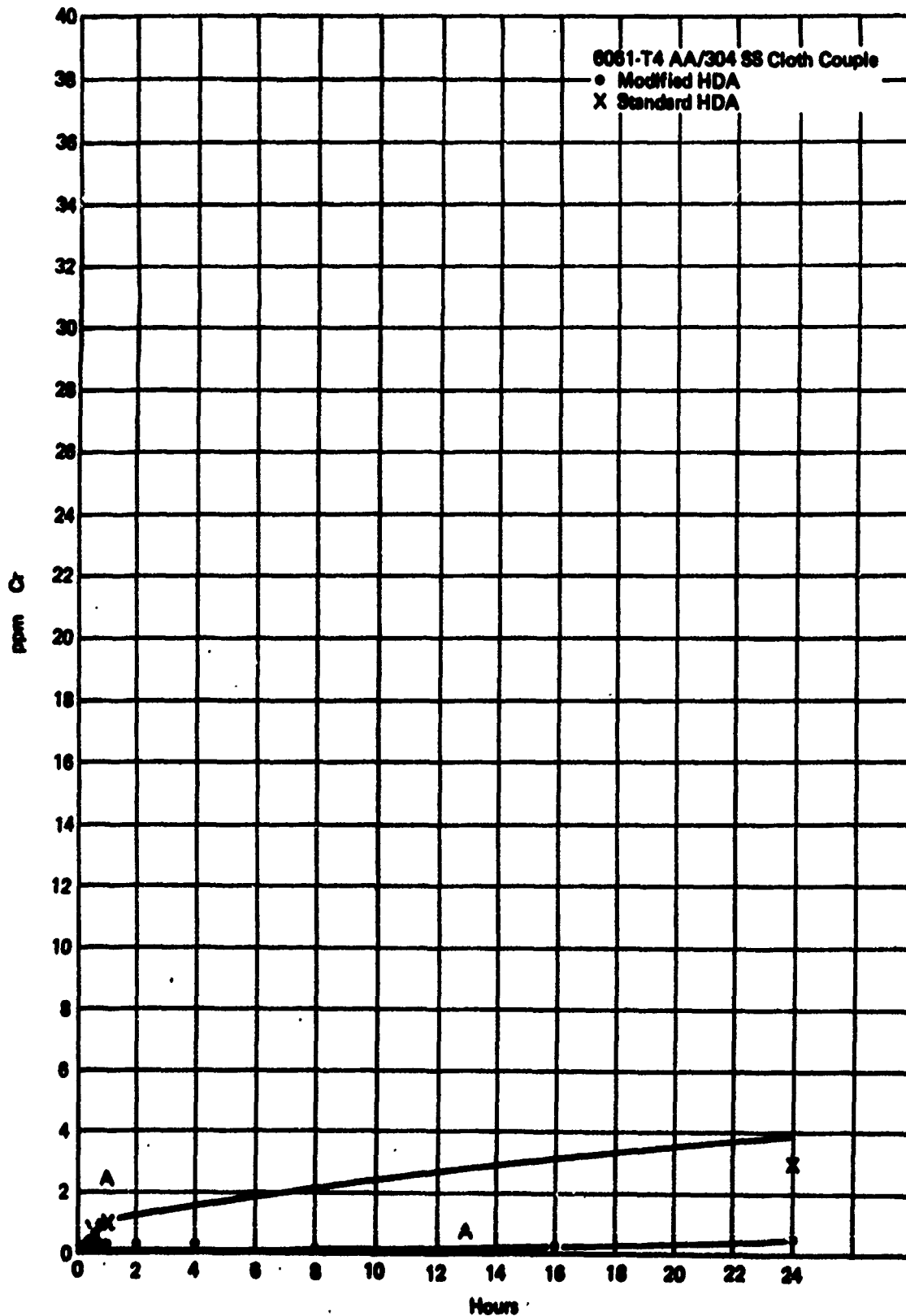


Figure 24. Passivation Tests - Chromium Buildup In Solution (1 of 2)



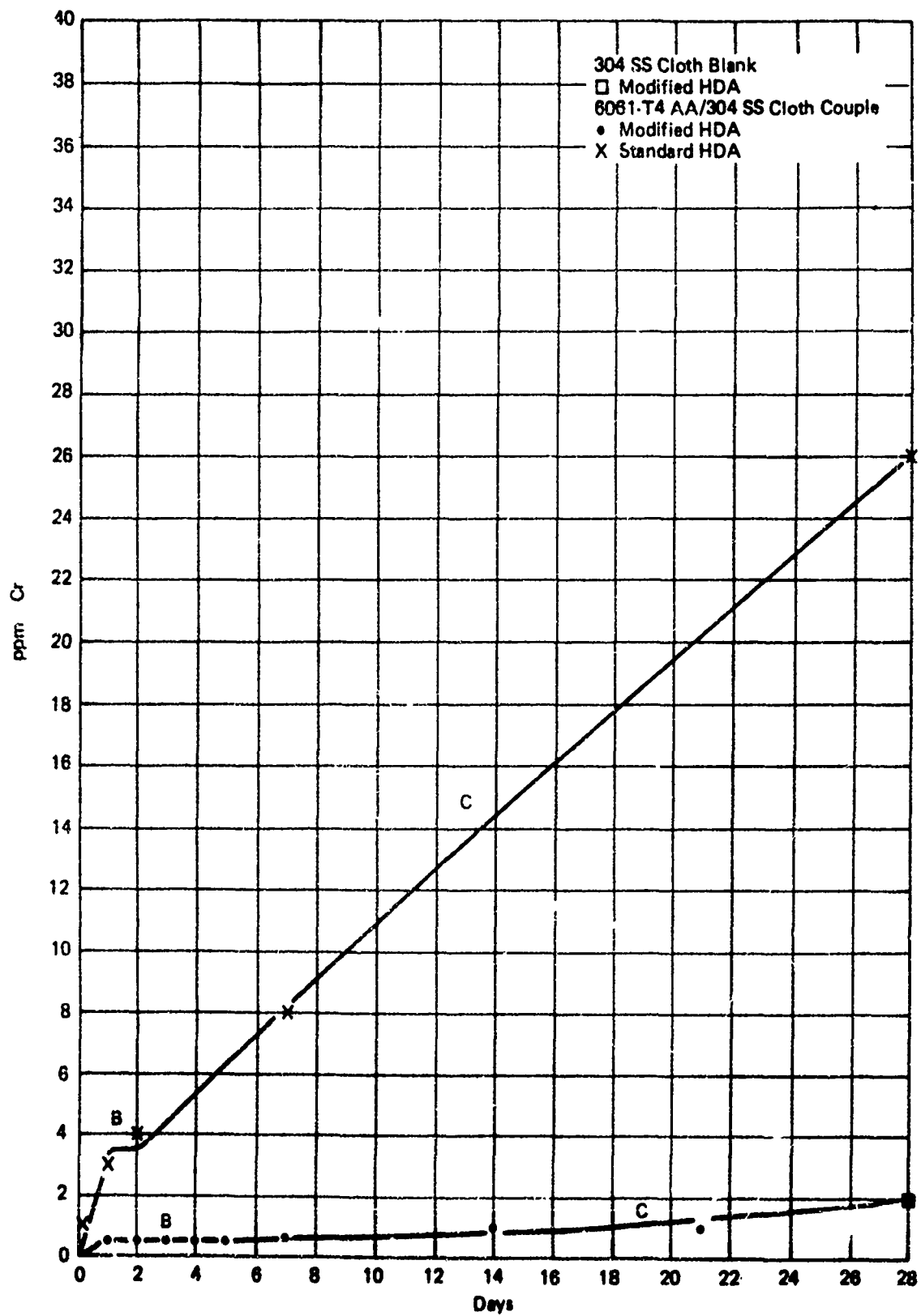


Figure 24. Passivation Tests - Chromium Buildup In Solution (2 of 2)

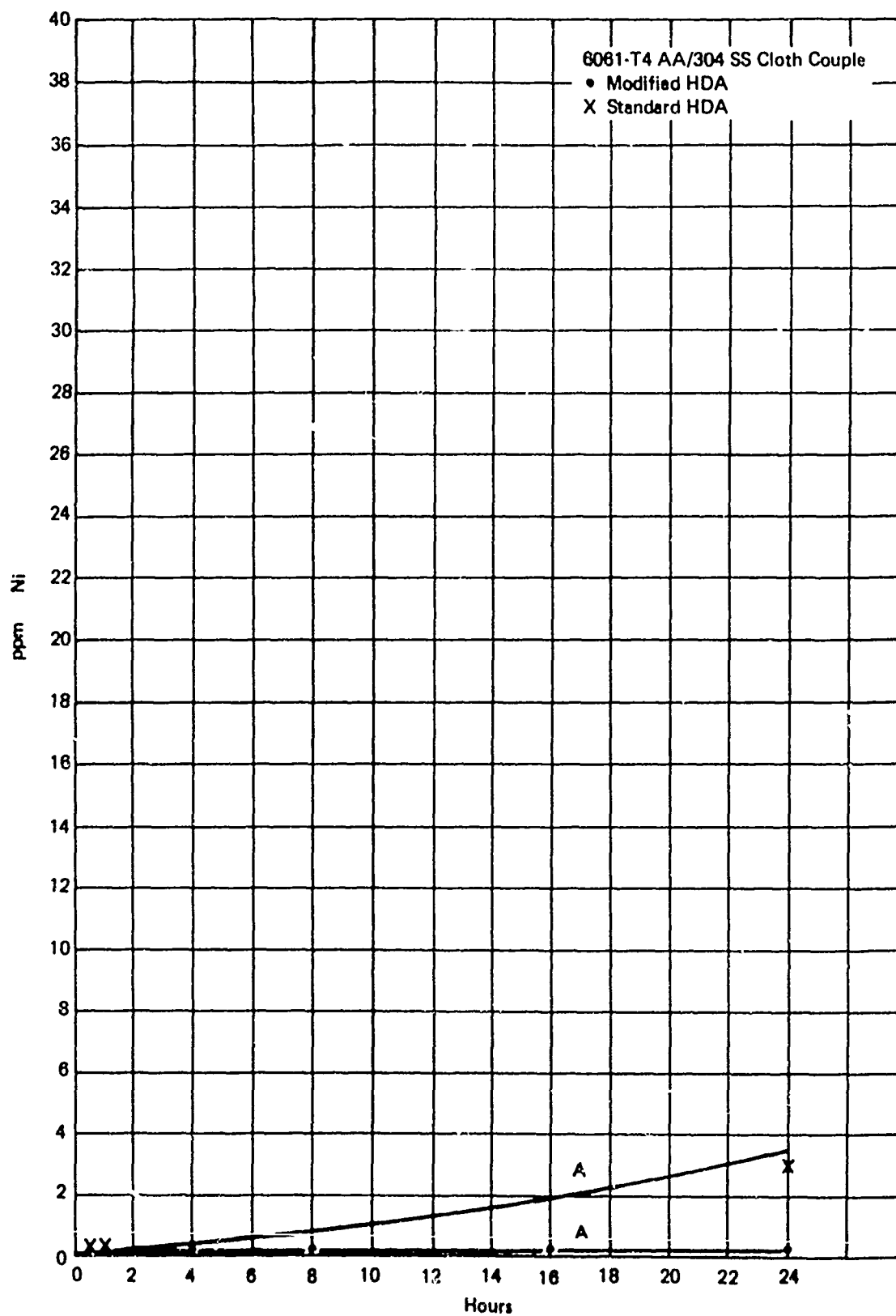


Figure 25. Passivation Tests - Nickel Buildup In Solution (1 of 2)

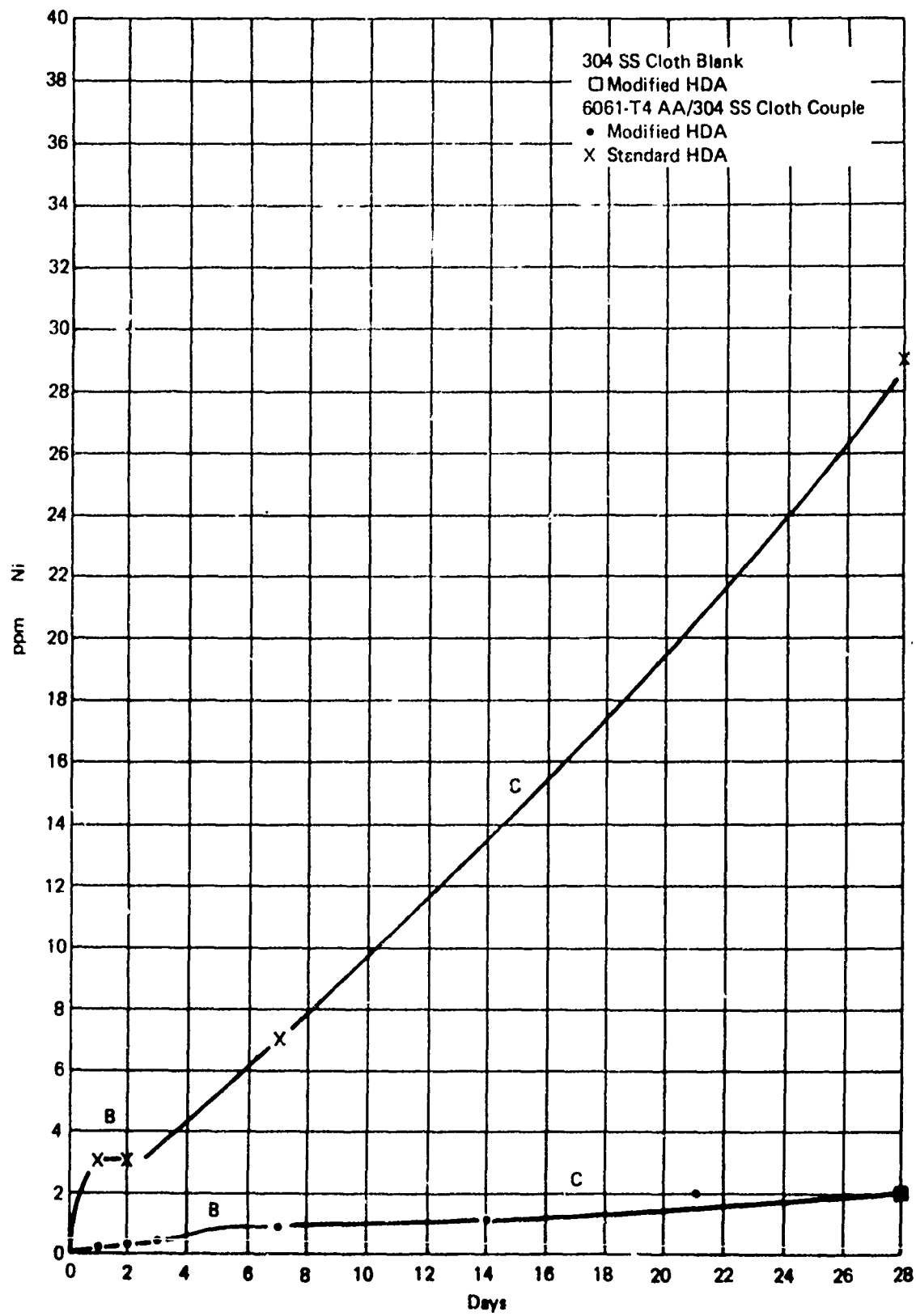


Figure 25. Passivation Tests - Nickel Buildup In Solution (2 of 2)

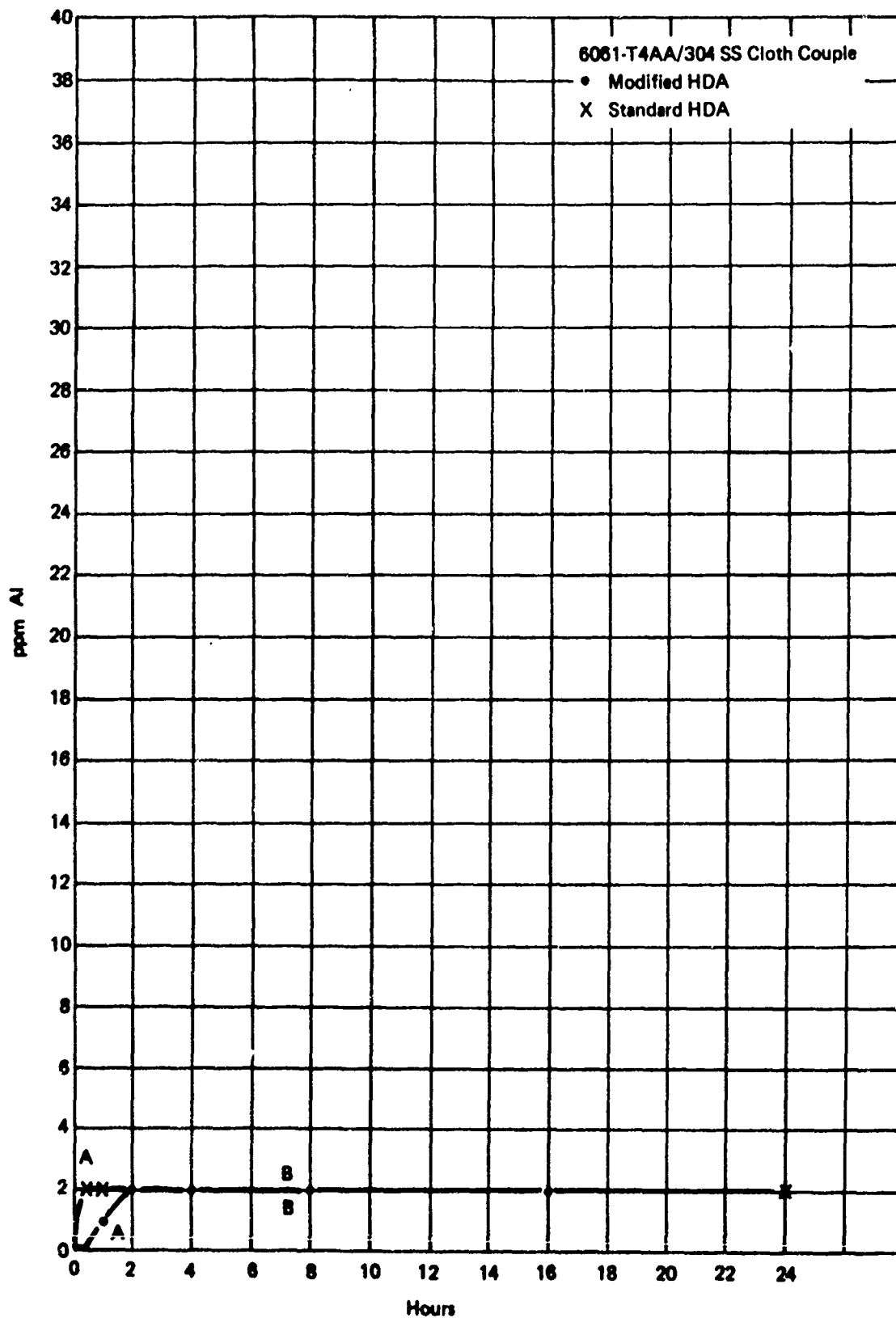


Figure 26. Passivation Tests - Aluminum Buildup In Solution (1 of 2)

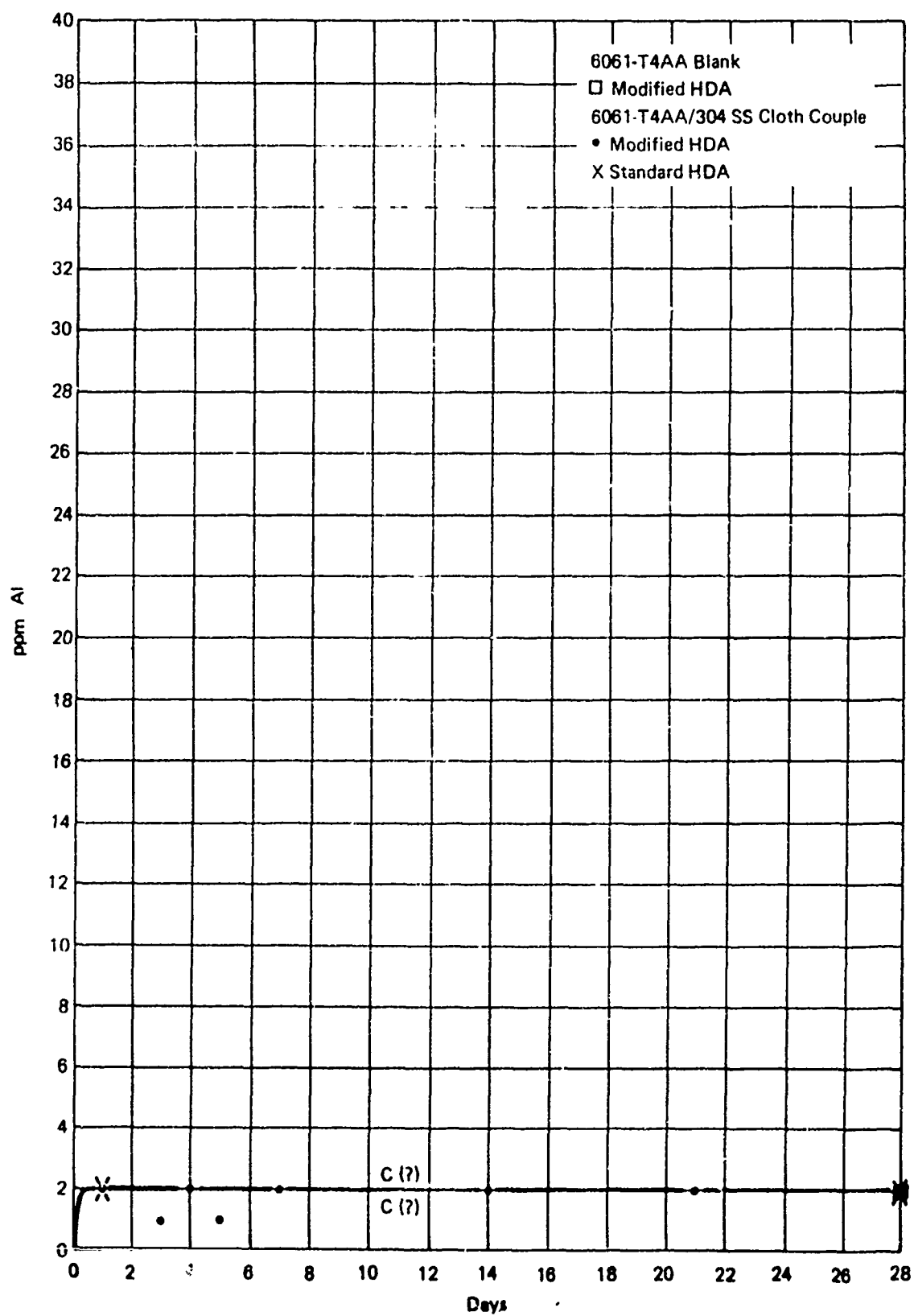


Figure 26. Passivation Tests - Aluminum Buildup In Solution (2 of 2)

### III. TECHNICAL DISCUSSION

#### 1.0 TASK 1 - CHARACTERIZATION OF MODIFIED HDA

##### 1.1 Density

The density of blends of Modified HDA containing different amounts of nitrogen dioxide and water was measured using pycnometers designed and built specifically for this program. The pycnometers included an aluminum bottle and a synthetic, sapphire capillary which were intended to provide an inert environment for the blends to be examined. The experimental procedure included the addition of a known weight of a given blend to a pycnometer, and confining the vapors of the blend with a stainless steel, ball valve, attached to the top of the capillary tube. The assembly was positioned in a thermostatically controlled water bath, and the elevation of the acid into the capillary was measured as a function of temperature. Test duration ranged from several hours to several days. Samples of acid were taken and analyzed at the beginning and the end of each test, to certify the validity of the density data in terms of a given acid composition. Density at a given test temperature was calculated from the weight of acid tested and its volume. The latter was calculated from the rise of the acid into the pycnometer capillary and previously determined calibration of volume as a function of height of liquid in the capillary at a given temperature. Further technical details and experimental data were given in Section II.

An indirect proportion was found between the density of a given blend of acid and temperature. As temperature was increased, there was a gradual decrease in density. When the densities of two blends of acid containing the same amount of water, but different amounts of nitrogen dioxide, were compared at the same temperature, relatively small differences were found. The trend was toward a maximum value at 44 wt %  $\text{NO}_2$ . This is in keeping with the designation of such a blend as maximum density acid. When comparisons were made of the densities of two blends of acid containing different amounts of water but the same amount of nitrogen dioxide, relative large differences were found at any given temperature. The lower the water content of the blend, the higher was the measured density. These effects of acid composition on density are evident upon inspection of curves 7, 8 and 9 in Figure 3. The curves correspond to blends of acid containing varying amounts of nitrogen dioxide, and the lowest water contents studied. The low water contents were reflected by the highest densities measured. The maximum density measured was a blend containing 42 wt % rather than 44 wt %  $\text{NO}_2$ , because the former blend contained a lower water content (0.1 wt %) than the latter (0.2 wt %).

The reliability of the experimental data upon which the foregoing deductions were based has been established in several ways. Besides the linearity of the density of a given blend of acid in a given pycnometer as a function of temperature, duplicate curves were obtained for one of the blends (77-10) which was subjected to separate sets of measurements in each of the two pycnometers prepared for tests.

Also received through chemical analyses made in support of density determinations was a better insight of aluminum pickling and passivation. Before assembly of the pycnometers, the aluminum bottles were pickled with aqueous solutions of acids normally used for this purpose. Analyses of the first Modified HDA blends used in pycnometer A/A (Stock No. 77-15) and in pycnometer B/B (Stock No. 77-12) disclosed relatively large increases in aluminum content. This was confirmed by the presence of particles in post test samples of acid. Subsequent tests showed relatively low levels of aluminum content by analyses, and clear acids by visual inspection. The

pickling solutions had produced a film on the interior of the aluminum bottles which was displaced with a more impervious film by continued exposure to Modified HDA.

Earlier comments about the validity of test procedures employed must be qualified, based on analyses made in support of measurements involving variations in the standard test procedure. Post test analyses revealed increases in water content for tests at high temperature, and an orthobaric density test. These tests were made with Stock No. 77-10, using both pycnometers. The pycnometers were only partly filled for the high temperature tests, and were evacuated after filling for the orthobaric density test. Both procedures trapped vapors in the pycnometer bottles and resulted in leaks during warm-up in the constant temperature water bath. The presence of additional water was evident from post test analyses. The density data were accordingly judged unreliable.

Further confidence in the validity of the standard test procedure was, however, provided by tests (Run 3, Stock No. 77-12, and Run 3, Stock No. 77-13) in which density was measured in the normal manner, after which the pycnometers were returned to the constant temperature water bath. The pycnometers were removed and reweighed three days later. No change in density was found for either solution. Post test analyses of the acids showed slightly higher than normal values for aluminum content, but no particulate matter was observable. There was no evidence of leakage or acid decomposition.

Further inspection of Figure 3 reveals that not only are the curves linear but also that they are parallel, i.e., have the same slope. One is justified, therefore, in extrapolating density for a given solution from one temperature to another, over the temperature range covered collectively by the experiments, using the slope  $-0.0020 \text{ gm/cm}^3/\text{°C}$  (grams per cubic centimeter per degree Celsius).

The slope measured for Modified HDA at Bell Aerospace Textron has been compared with data in the literature for other types of HDA. The comparative data are given in Table 27. Close agreement is observed in each case. Although Reference 4 reports on tests with anhydrous acids, data obtained in this study indicate that, in fact, the earlier blends contained approximately 0.2 wt % water.

TABLE 27. SLOPE OF HDA DENSITY CURVES

Type of HDA	Slope $\text{gm/cm}^3/\text{°C}$	Reference
Uninhibited	-0.0019	4 <sup>a</sup>
Standard	-0.0021	5 <sup>b</sup>
Standard	-0.0019	6 <sup>c</sup>
Modified	-0.0020	This Work

<sup>a</sup>Reference 4. "Equilibrium Pressures of Solutions of Nitrogen Dioxide in High Concentrations of Anhydrous Nitric Acid and Corresponding Densities," A. Klemenc and J. Rupp, Journal of Inorganic and Analytical Chemistry, 194, 51 (1930).

<sup>b</sup>Reference 5. "Results of Physical Characterization of IMDFNA," E.A. Lawton, Rocketdyne, Letter Report 70RC9682, 2 September 1970.

<sup>c</sup>Reference 6. "A Pycnometer Technique For Density Determination of High Density Acid," L.A. Dec, Air Force Rocket Propulsion Laboratory, Technical Memorandum 75-16, September 1975.

The effects found at Bell Aerospace Textron of changing nitrogen dioxide content at low water content were the same as found in Reference 4. That is, acid containing 42 wt % nitrogen dioxide is more dense at a given temperature than acid containing 46 wt % nitrogen dioxide. At higher concentration of water, the trend is reversed, as reported in Reference 6 and found in this work.

A comparison of high density acids containing similar concentrations of nitrogen dioxide and water, at a constant temperature, 60°F (15.6 °C), provides an indication of the relatively small effect exerted by the presence of a given corrosion inhibitor on the density of the resulting blends. These data are shown in Table 28. Approximate values are given for the referenced data. More precise definitions of the effect of changing corrosion inhibitor would require additional determinations with acids with controlled amounts of nitrogen dioxide and water.

TABLE 28. HDA DENSITY AS A FUNCTION OF CORROSION INHIBITOR

Corrosion Inhibitor	Temperature		Density gm/cm <sup>3</sup>	Reference
	°F	°C		
None	60.0	15.6	~ 1.6492	4
0.8 wt % HF	60.0	15.6	~ 1.6445	5
0.4 wt % HF	60.0	15.6	~ 1.6385	6
0.5 wt % PF <sub>5</sub>	60.0	15.6	1.6485	This Work

## 1.2 Specific Gravity and Buoyancy Effect

A set of tests was conducted with the object of comparing the density of Modified HDA as derived from specific gravity data, obtained with a hydrometer, with the density of the same samples, as determined directly with a pycnometer. The difference in density of a given sample as determined by the one method compared to the other is referred to as the "buoyancy effect" of the hydrometer.

The hydrometer selected for the comparisons was calibrated with an aqueous solution of phosphoric acid before and after measurements of the specific gravity of the Modified HDA blends. The post test calibration was made to allow corrections for minor etching of the hydrometer during exposure to Modified HDA. The calibrations and measurements were carried out at 60°F (15.56°C). With one exception, the measurement of specific gravity followed a successful determination of density, with a pycnometer, and chemical analysis, confirming constant composition of the blend for both types of measurement. The exception was a case in which density was rerun successfully after specific gravity had been measured.

Nine blends of Modified HDA were subjected to comparative measurements. Stock No. 77-13 was the blend for which specific gravity was measured before satisfactory density data had been obtained. The change in sequence was proven to be immaterial by a rerun of specific gravity after the successful density determination. The specific gravity measurements agreed within ±0.0001 units, matching the accuracy of the method. The specific gravity data for Stock No. 13 were, however, doubtful in another respect. The blend contained 44 wt % NO<sub>2</sub> and had exhibited the maximum density for the set, (Stock No. 77-12 to 77-14). Stock No. 77-12 contained 42 wt % NO<sub>2</sub>. Stock No. 77-14 contained 46 wt % NO<sub>2</sub>. Since water content was constant at 1.0 wt %, the order of measured densities was as expected. The specific gravity of the blends, however, increased with increasing nitrogen dioxide content. The increase is attributed to the "buoyancy effect".



The magnitude of the "buoyancy" effect for a given Modified HDA blend was determined by calculating the density of the blend at 60°F (15.56°C) from the measured value for specific gravity at this temperature. The calculation involved multiplication of the measured value for specific gravity by the density of water, 0.99902 gm/cm<sup>3</sup>. The numerical difference between the measured and derived values for density of a given blend is the precise "buoyancy effect".

The density, specific gravity and "buoyancy effect" for each Modified HDA blend studied are shown in Table 6. It will be noted that an increase in water content for Modified HDA resulted in decreased values for density and specific gravity. Without exception, density derived from a hydrometer reading was higher than density determined directly with a pycnometer. The "buoyancy effect" varied in a random manner from +0.0013 to +0.0054 gm/cm<sup>3</sup>. The fact that no pattern was obvious in the variations, upon systematic changes in acid composition, reduces the value of hydrometer readings. The fact that an error of 0.3% in derived density was demonstrated makes the use of hydrometers for obtaining data for rocket engine performance calculations unreliable. These calculations involve conversion of measured volumetric flow of propellant to mass flow, on the basis of the density of the propellant. A pycnometer of practical design is recommended for obtaining the required data.

### 1.3 Vapor Pressure

Preliminary data for the vapor pressure of Modified HDA were reported in Reference 7<sup>a</sup>. The data were obtained by charging an analyzed sample of acid into a Teflon lined, aluminum cylinder, fitted with a pressure transducer and thermocouple. The latter were attached to a recorder. The test vessel was partially immersed in a constant temperature water bath. After pressure readings stabilized, the temperature of the bath was raised to a higher level, and pressure was again allowed to stabilize. As expected, the pressure increased with each increase in temperature. Parallel runs with a smaller amount of acid in a second test vessel of the same type gave lower pressure readings at any given temperature. The smaller amount of acid loaded left a larger ullage (vapor phase). This suggested that the total pressure measured contained a variable component. This component was thought to arise from partial decomposition of the acid sample according to the equation.



In a closed system, at a given temperature, the nitric acid would exert a definite vapor pressure. Some of the O<sub>2</sub> (oxygen) generated in reaching equilibrium would remain in solution. Most of the O<sub>2</sub> would enter the gas phase and exert pressure in accord with PVT (Pressure Volume Temperature) relationships. This pressure is referred to as decomposition pressure. The larger the ullage, the smaller would be the decomposition pressure, at a given temperature. Data taken for the high ullage (90%) vessel are shown in Figure 27. A relatively large average deviation is indicated for the measurements.

Shown for comparison in Figure 27 are data points from this work, taken at high ullage, and a common temperature; for stock solutions containing the same amount of H<sub>2</sub>O (water), somewhat more PF<sub>5</sub> (phosphorous pentafluoride) but significantly smaller and larger amounts of NO<sub>2</sub>. The original curve is displaced approximately 2 psia above the currently accepted locus.

---

<sup>a</sup>Reference 7. "Modified HDA Studies," H. Ph. Heubusch, Bell Aerospace Textron, AFRPL-TR-73-77, October 1973.

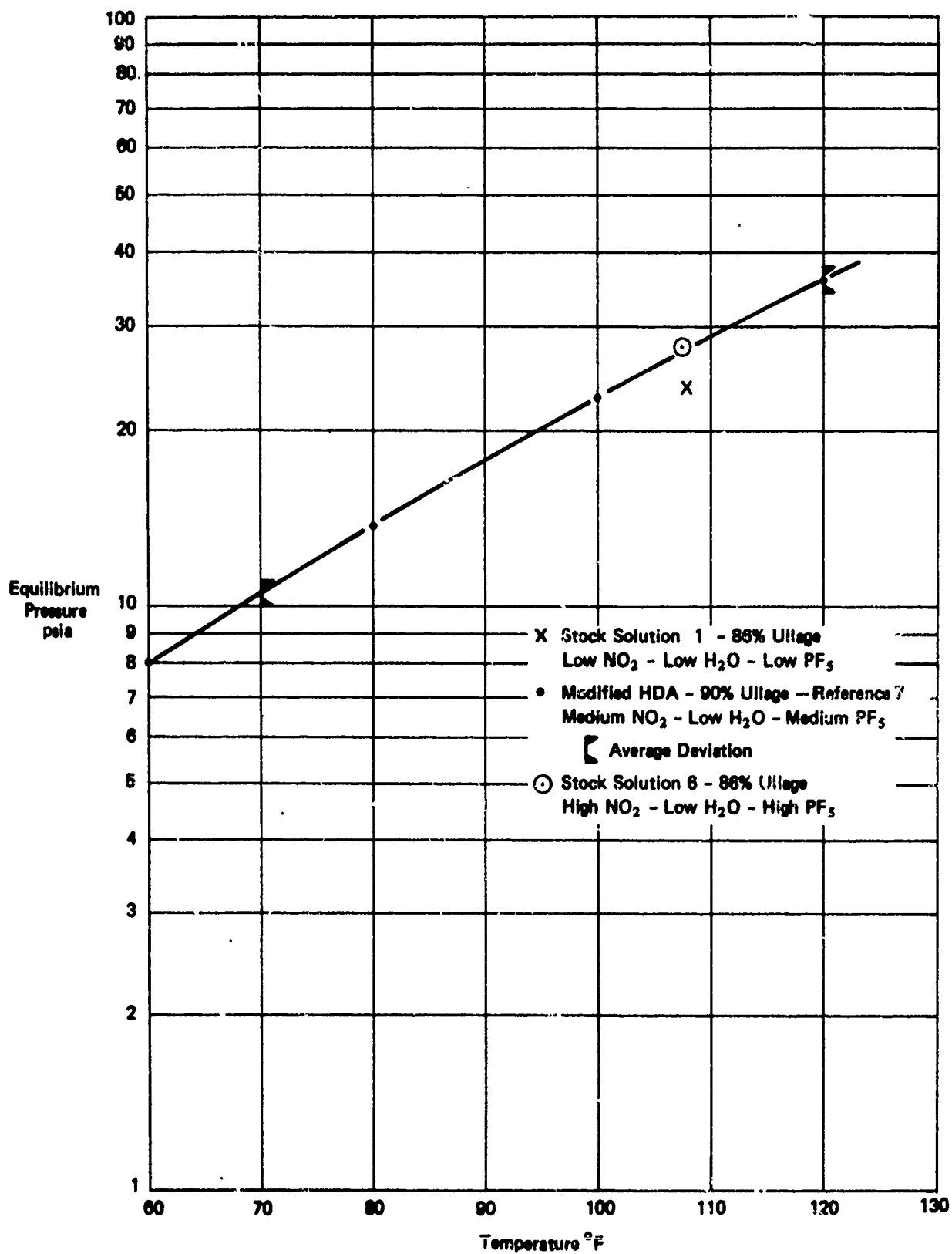


Figure 27. Vapor Pressure as a Function of  $\text{NO}_2$  Content at High Ullage

A similar comparison was made between Standard HDA and Modified HDA. Data from Reference 5, for vapor pressure as a function of temperature of a sample of Standard HDA containing a high concentration of the corrosion inhibitor HF (Hydrofluoric Acid) and a medium concentration of  $\text{NO}_2$ , are plotted in Figure 28. Also plotted are data from this work for solutions containing an equivalent amount of the corrosion inhibitor  $\text{PF}_3$  and smaller and larger amounts of  $\text{NO}_2$ . The  $\text{H}_2\text{O}$  content was the same for all three stock solutions represented. The locus of the Standard HDA curve is higher than would be predicted, on the basis of the higher boiling point for HF than for  $\text{PF}_3$ , and the smaller reported value for  $\text{NO}_2$  content. Measurements of the Vapor Pressure of Standard HDA under conditions used in this work would be required before further conclusions could be drawn.

The stock solutions mentioned in the forgoing discussion were part of a two-cube factorial experiment design used for this work. One advantage of such a design is the fact that with eight solutions containing high and low concentrations of three components judged responsible for variations in a property such as vapor pressure, one can obtain data which directly identifies the controlling variable(s). Another advantage is the fact that the exact concentration of each component need not be known. What is more important is a relatively large difference between high and low concentrations, and relatively close agreement in the concentration of a given constituent at each extreme. These facts proved especially valuable during this work because of difficulties encountered in fixing the exact concentration of nitrogen dioxide (the controlling variable) for each solution. As previously explained in Section II, relatively large losses of nitrogen dioxide occurred during the evacuation, expansion and resampling steps of each vapor pressure determination. The net result was an uncertainty in the exact nitrogen dioxide compositions for the stock solutions being tested. The uncertainty was greatest with stock solutions containing initially high concentrations of  $\text{NO}_2$ . The magnitude of this uncertainty for a given stock solution has been better defined by further consideration of the data in Table 9, covering vapor pressure experiments.

After stock solution P, containing low concentrations of  $\text{NO}_2$  and  $\text{PF}_3$ , but a high concentration of  $\text{H}_2\text{O}$  had been examined at increasing temperatures, and increasing ullage, at the highest temperature, it was allowed to cool, and a set of data were obtained to complete Experiment 1. Comparison of the pressures measured at low temperature, at the beginning and end of the experiment, showed a decrease from 10.5 to 9.8 psia. This decrease corresponds to an increase in ullage from 58 to 86%.

Similar reasoning applied to Experiment 2 performed with stock solution JB explains a decrease in pressure from 12.2 to 11.7. Temperatures at the beginning and end of the experiment were higher than for Experiment 1. When an adjustment for this fact was made, lower pressures were realized for stock solution JB, which contained a similar concentration of  $\text{NO}_2$ , but a lower concentration of  $\text{H}_2\text{O}$ . The experiment was terminated at the evacuation step of the standard vapor pressure procedure, to evaluate loss of nitrogen dioxide due to the evacuation step. The relatively low value previously reported was attributed largely to the low concentration of  $\text{NO}_2$  in the stock solution, and in part to the relatively short duration of the test (4 hours).

Experiment No. 3 was performed to determine the loss of nitrogen dioxide associated with resampling upon completion of a vapor pressure run. No evacuation steps were performed. Therefore, the pressure measured after thermal equilibrium was established included pressure from nitrogen, originally in the test vessel, which was not displaced during propellant loading. The effect was to raise the pressure from approximately 12 psia as noted in Experiment 2 to 19.6 psia. The magnitude of this increase mandated removal of nitrogen before equilibrium pressure runs.

Evacuation steps were, however, waived for Experiment 4, which was performed to determine the loss of nitrogen dioxide during the expansion steps of the standard procedure. The ex-

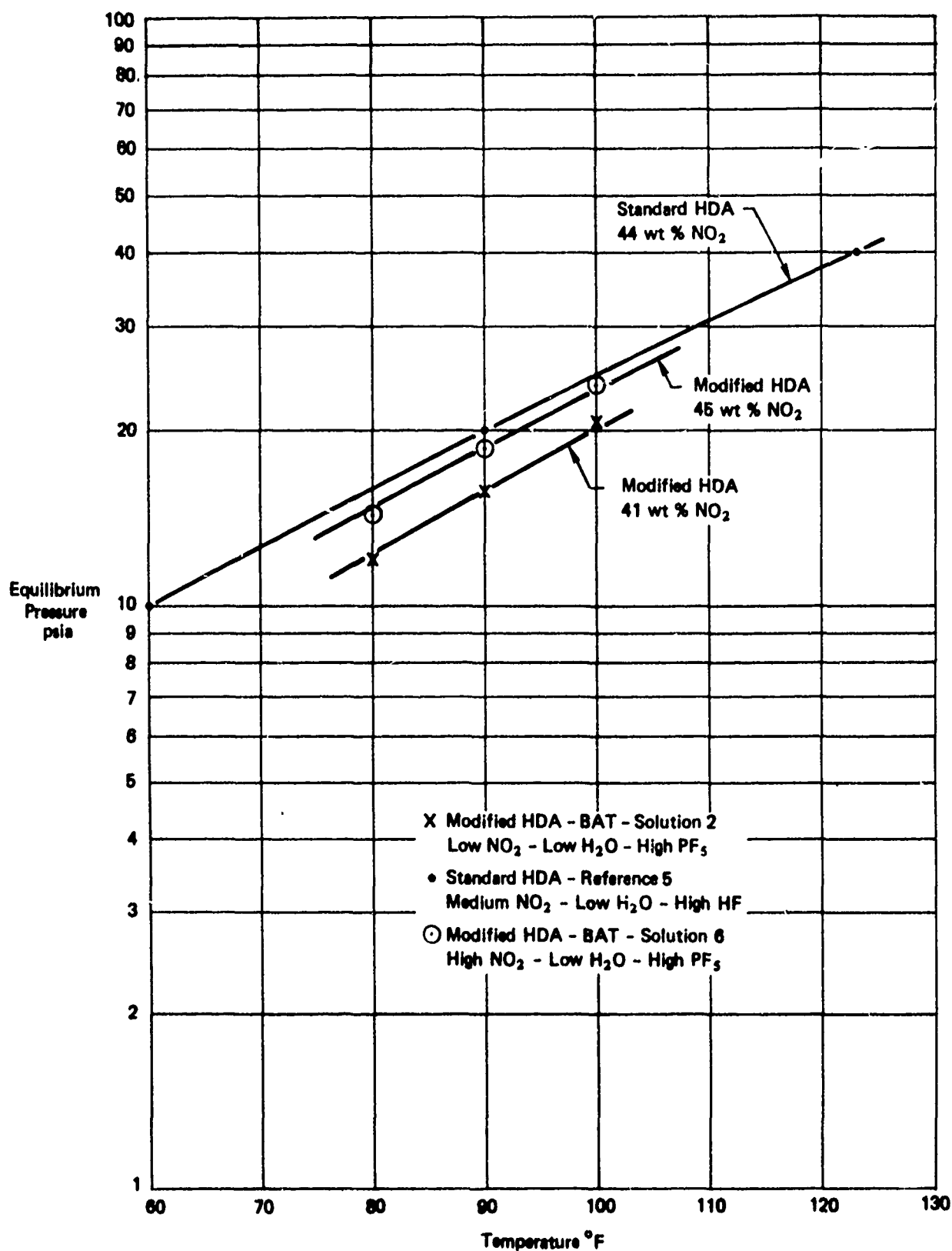


Figure 28. Vapor Pressure of Modified HDA Compared to Standard HDA

pansions were carried out at high temperature. The presence of nitrogen raised the pressure before expansion to 29.8 psia, compared with a pressure of approximately 22 psia measured during Experiment 1. A further comparison between the two experiments involved calculations of the loss of  $\text{NO}_2$  due to expansion during Experiment 1, with the loss measured in Experiment 4. The data are summarized in Table 29.

TABLE 29.  $\text{NO}_2$  LOSS ON EXPANSION

Source	Wt %	Comments
Calculated	0.6	from Data Experiment 1 Assumed from $\text{NO}_2(\text{g})$
Measured	0.6	Experiment 4

A loss of 0.6 wt %  $\text{NO}_2$  was calculated from the equation

$$w = \frac{PVM}{RT} \quad (2)$$

where

- w = weight of  $\text{NO}_2$ , gm
- P = pressure after final expansion, atm
- V = vapor volume after final expansion, liter
- M = molecular weight of  $\text{NO}_2$ , gm
- T = temperature after final expansion, °K (Absolute Temperature)
- R = gas constant, liter atmos./mole °K

This equation assumed that the pressure measured was due principally to gaseous  $\text{NO}_2$ . The contributions of oxygen, nitric acid, etc. were considered to be negligible. The close agreement between calculated and measured values substantiated the assumption.

Another calculation made using data from Experiment 1 and the gas laws was performed to compare measured decreases in pressure after expansions, as reported in Table 10, with the results which would be obtained from simple expansion of a fixed amount of gas. The equation used was

$$P_1 V_1 = P_2 V_2 = P_3 V_3 \text{ at } T_c \quad (3)$$

where

- $P_1$  = pressure of vapors in test vessel  $V_1$  preceding expansion, atm
- $V_1$  = volume of vapors in test vessel  $V_1$  preceding expansion, liter
- $P_2$  = calculated pressure of vapors, after first expansion, atm
- $V_2$  = volume of vapors in test vessels  $V_1$  and  $V_2$ , after first expansion, liter
- $P_3$  = calculated pressure of vapors, after second expansion, atm
- $V_3$  = volume of vapors in test vessels  $V_1$ ,  $V_2$ , and  $V_3$  after second expansion, liter
- $T_c$  = constant temperature, during experiment, °K

The results are summarized in Table 30.

TABLE 30. CALCULATED PRESSURE OF VAPORS UPON EXPANSION

Step	Pressure, atm	
	Calculated	Measured
Before Expansion	—	1.54
After First Expansion	0.58	1.46
After Second Expansion	0.35	1.40

The large differences between calculated and measured values are attributed to the constant increment of vapor pressure in the equilibrium pressures measured. The relatively small differences in measured values are attributed to expansion of  $O_2$ , formed by decomposition of  $HNO_3$ , (nitric acid), and the relatively low solubility of  $O_2$  in the acid.

Experiment 5 was similar to Experiment 2 in that the loss of  $NO_2$  during the evacuation steps of the standard vapor pressure procedure was to be determined. The experiments differed in that Stock Solution 5, containing a high concentration of  $NO_2$  (45 wt %), was used for Experiment 5. As previously reported, the higher, initial  $NO_2$  content was associated with a larger loss of  $NO_2$  on evacuation. Comparison of the pressures measured at thermal equilibrium, after evacuation, disclosed the relatively high  $NO_2$  content of Stock Solution 5. At  $80.8^\circ F$  ( $27.14^\circ C$ ), a pressure of 14.2 psia was measured for Stock Solution 5, compared with approximately 11.7 psia for Stock Solution JB, which contained 40 wt %  $NO_2$ .

Further information concerning the loss of  $NO_2$  during the expansion steps of the standard vapor pressure procedure were obtained by comparing the pressure at the end of each vapor pressure run with the pressure taken from the vapor pressure curve at the temperature at the end of the run. The comparative data are shown in Table 31.

TABLE 31  
PRESSURE DROPS DUE TO EXPANSION

Run No.	Temperature		Pressure, Psia		
	$^\circ F$	$^\circ C$	Before Expansion	After Expansion	$\Delta P$
1	75.6	24.2	10.6	9.8	0.8
2	81.2	27.3	12.5	11.8	0.7
3	83.0	28.3	13.4	12.7	0.7
4	76.4	24.7	11.7	11.0	0.7
5	76.8	24.9	13.0	12.2	0.8
6	77.1	25.0	13.2	12.3	0.9
7	—	—	—	—	—
8	75.6	24.2	13.2	12.3	0.9

Acquisition of data for Run 7 was waived to expedite repair of a thermistor lead broken during post test operations. An average decrease of 0.8 psia was noted for the other experiments.

As mentioned in Section II, with reference to Table 14, the concentrations of nitrogen dioxide is a controlling variable over the vapor pressure of Modified HDA. Further consideration of the table shows no measurable difference in pressures exerted by solutions differing only in  $\text{PF}_5$  content. Compare the data for Stock Solutions 1 and 2, as an example. The addition of water, on the other hand, results in an increase in pressure at any given temperature. Compare the data for Stock Solutions 1 and 3, as an example. The data for Stock Solution 4 are irregular in that a somewhat higher  $\text{NO}_2$  content was used than for Stock Solutions 1 - 3. This gave higher pressures and obscured further comparisons of the effects of  $\text{H}_2\text{O}$  and  $\text{PF}_5$ .

The power of  $\text{NO}_2$  as a controlling variable is shown graphically in Figure 28. This is a plot of vapor pressure for two stock solutions (1 and 5), containing equal amounts of  $\text{H}_2\text{O}$  and  $\text{PF}_5$ , but different amounts of  $\text{NO}_2$ . The curve for Stock Solution 5, containing a high concentration of  $\text{NO}_2$ , lies well above the curve for Stock Solution 1, containing a low concentration of  $\text{NO}_2$ . The curve for Stock Solution 4 (Figure 12), containing slightly more  $\text{NO}_2$  than Stock Solution 1 falls just above the lower curve in Figure 29.

The relatively small control concentrations of  $\text{N}_2\text{O}$  and  $\text{PF}_5$  exerted over vapor pressure is illustrated in Figure 30. This figure contains plots for the four Stock Solutions (5 - 8) containing high  $\text{NO}_2$  content. The curves are closely bunched and cross over one another at some points.

As mentioned in Section II, concerning Table 15, total pressure drop through expansions carried out during vapor pressure runs were similar for the various stock solutions because their compositions and the amount of decomposition involved fall in relatively narrow bands. Further inspection of the tabulated data shows that pressure drops for the first expansion averaged 0.04 atm, and for the second expansion, 0.02 atm. This constancy of data is another point in support of the foregoing conclusions.

Data from each vapor pressure run were used to calculate the decomposition pressure of Modified HDA at the temperature at which vapors were expanded from one test vessel to another. The rationale employed is shown in Figure 31. This figure contains the results for Stock Solution 1, which exhibited average pressure drops. In summary, the calculation provided data for components of the measured equilibrium pressures, in accordance with the equation:

$$\Rightarrow P = VP + DP \text{ at } T_c^\circ \quad (4)$$

where:  $\Rightarrow P$  = equilibrium pressure, measured, atm  
 $VP$  = vapor pressure, by difference, atm  
 $DP$  = decomposition pressure, calculated, atm  
 $T_c^\circ$  = temperature during expansion,  $^\circ\text{K}$

From the experimental data gathered through the first expansion the following results were obtained for equation (4):

$$\begin{aligned} \Rightarrow P &= VP + DP \text{ at } T_c^\circ \\ 1.64 &= 1.58 + 0.06 \text{ at } 315.4^\circ\text{K} \end{aligned} \quad (5)$$

The experimental data, gathered through the first expansion, were then used to predict the equilibrium pressure at the end of the second expansion. A pressure of 1.61 atm was predicted.

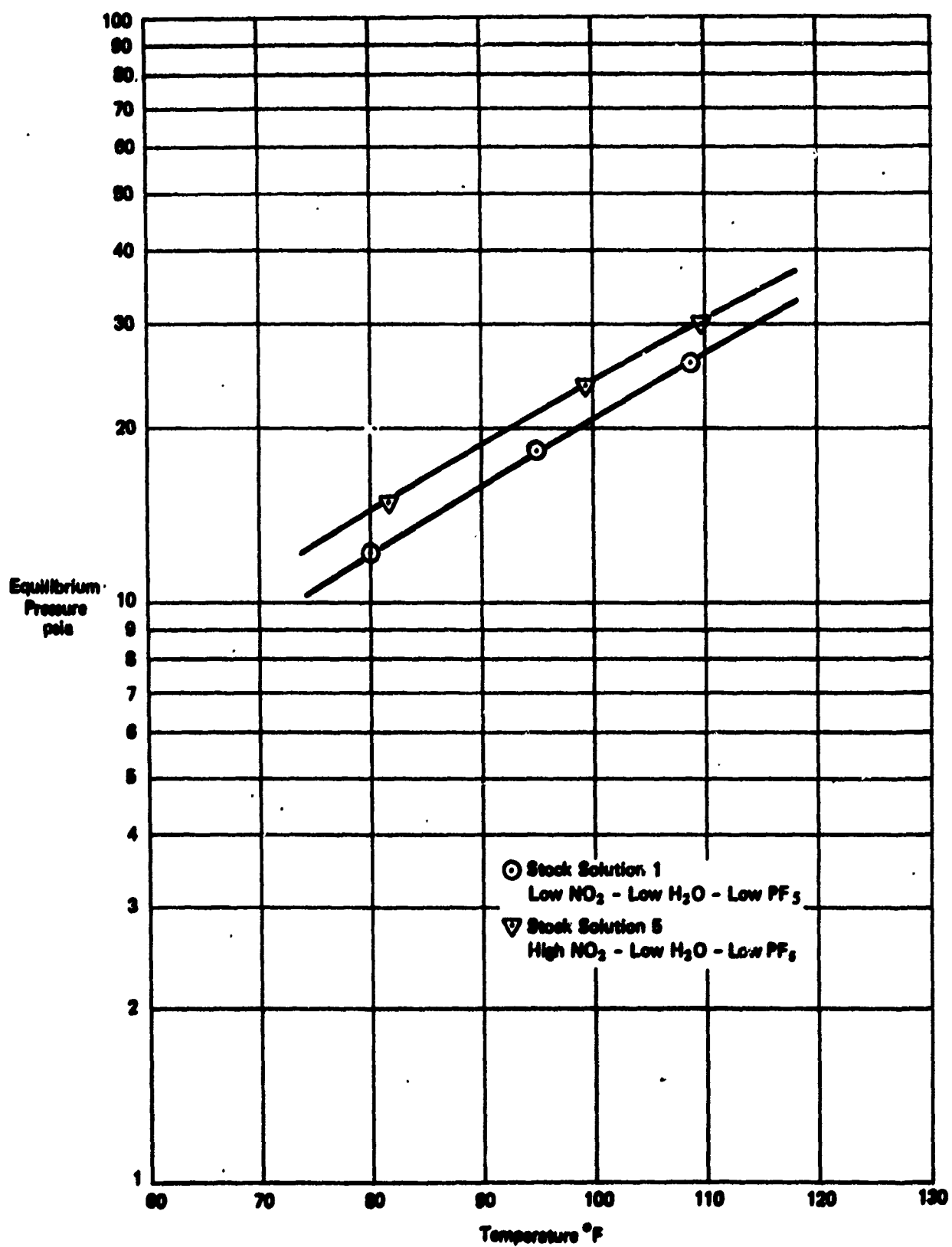


Figure 29. Vapor Pressure of Modified HDA as a Function of  $\text{NO}_2$  Content



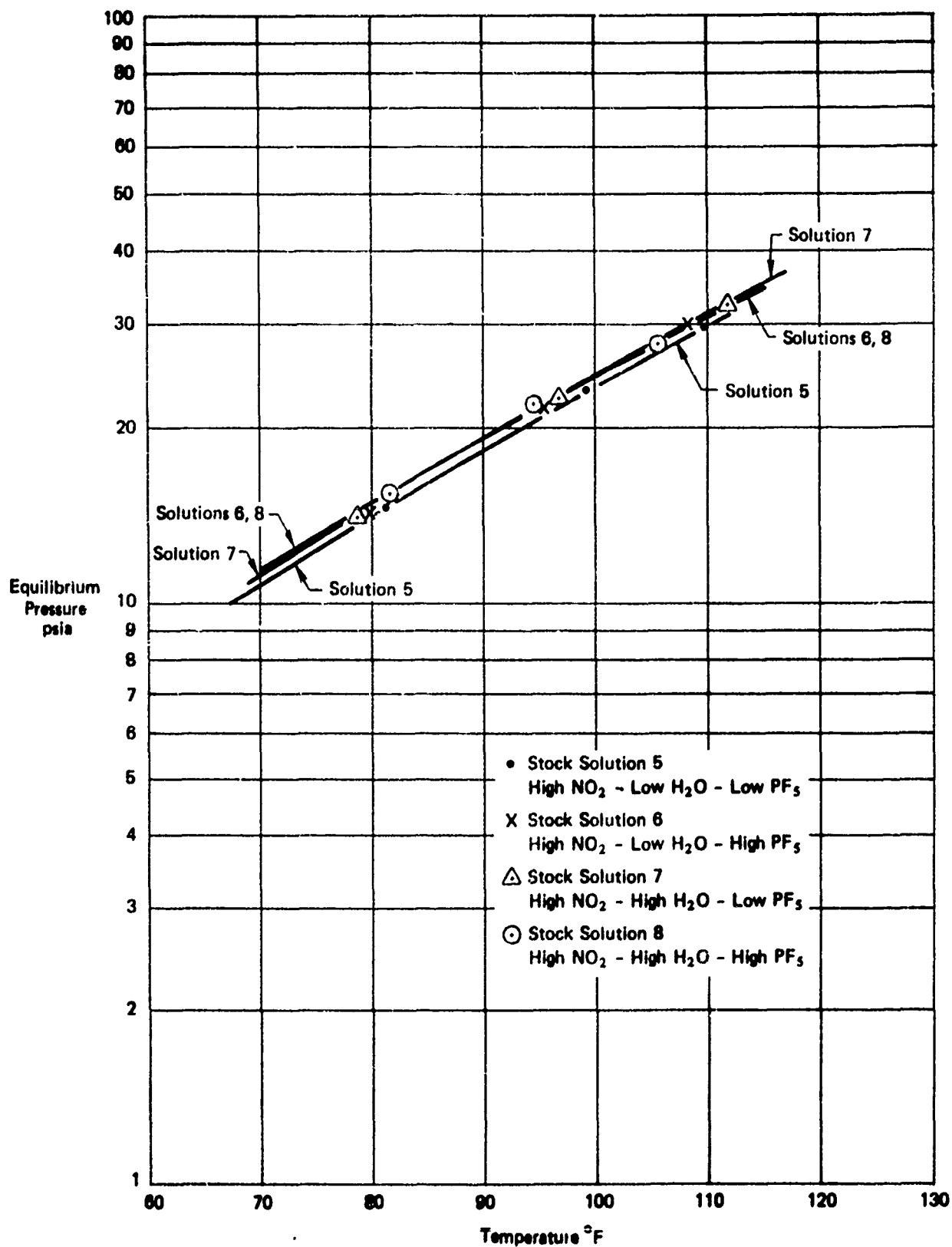


Figure 30. Vapor Pressure of Modified HDA as Functions of H<sub>2</sub>O and PF<sub>5</sub> Contents

Data from Run 4 with Stock Solution 1 (Table 13)

1. Assume liquid and vapors at equilibrium in  $V_1$  at  $T_3^o$  ( $108.7^\circ\text{F} = 42.6^\circ\text{C} = 315.8^\circ\text{K}$ )
2. Assume vapors =  $\text{O}_{2(g)}$  (gaseous oxygen)
3. Calculate moles of  $\text{O}_{2(g)}$  in  $V_1$  at  $T_3^o$

$$\text{Volume HDA} = \frac{\text{gm loaded}}{\rho \text{ as loaded}} = \frac{167 \text{ gm}}{(1.6245_{19.8^\circ} + (20.9^\circ \times 0.0020)) \text{ gm/cm}^3} = 100.2 \text{ cm}^3$$

$$\text{Volume HDA} = \frac{\text{gm loaded}}{\rho \text{ at } T_3^o} = \frac{167 \text{ gm}}{(1.6245_{19.8^\circ} - (22.8 \times 0.0020)) \text{ gm/cm}^3} = 105.8 \text{ cm}^3$$

$$\text{Volume } \text{O}_{2(g)} = \text{Volume } (V_1 - \text{HDA}) = 237.2 - 105.8 = 131.4 \text{ cm}^3 = 0.131 \text{ L}$$

$$P_1 = 52.2'' \text{ Hg} \times 0.49 \text{ psia}'' \text{ Hg} \div 14.7 \text{ psia/atm} = 1.74 \text{ atm}$$

$$n = \frac{PV}{RT_3^o} = \frac{1.74 \times 0.131}{0.08205 \times 315.8} = 0.0088 \text{ moles}$$

4. Assume no further decomposition of acid at  $V'$ ,  $T_3^o$

Assume  $VP \equiv p_{\text{NO}_2}$  = Vapor Pressure

Assume  $DP \equiv p_{\text{O}_2}$  = Decomposition Pressure

Assume  $p_{\text{O}_2} \propto \frac{1}{V}$  and no more oxygen comes out of HDA during expansion

5. Calculate  $p_{\text{O}_2}$  at  $V'$ ,  $T_3^o$

$$V' = V_1 + V_2 = 0.131 + 0.239 = 0.370 \text{ L}$$

$$p_{\text{O}_2} = \frac{nRT_3^o}{V'} = \frac{0.0088 \times 0.08205 \times 315.8}{0.370} = 0.616 \text{ atm}$$

6. Calculate  $\Delta P = (3) - (5) = 1.74 - 0.62 = 1.12 \text{ atm}$

7. Calculate  $\Delta P = P_1 - P'_1 = 1.74 - 1.64 = 0.10 \text{ atm}$

8. Recalculate  $n$  from  $P_1 - P'_1$  and (3) - (5)

$$\frac{0.0088}{1.12} = \frac{n'}{0.10}$$

$$n' = 0.00079 \text{ moles } \text{O}_2$$

9. Calculate  $p_{\text{O}_2}$  in  $V_1$  at  $T_3^o$

$$p_{\text{O}_2} = \frac{n'RT_3^o}{V_1} = \frac{0.00079 \times 0.08205 \times 315.8}{0.131}$$

$$= 0.16 \text{ atm} \equiv DP \equiv 2.4 \text{ psia}$$

Figure 31. Equilibrium Pressure Calculations (1 of 2)

10. Calculate  $P_{\text{NO}_2}$  in  $V_1$  at  $T_3^\circ$   
 $P_{\text{NO}_2} = \Rightarrow P \cdot p_{\text{O}_2} = 25.6 \cdot 2.4$   
 $= 23.2 \text{ psia} \equiv VP \equiv 1.58 \text{ atm}$
11. Calculate  $P_{\text{O}_2'}$  in  $V'$  at  $T_3^\circ$  where  $V' = V_1 + V_2$   
 (No new assumptions)  
 $P_1 V_1 = P_2 V'$  at  $T_3^\circ = T'$  (after first expansion)  
 $(0.16) (0.132) = p_{\text{O}_2} (0.131 + 0.239) \text{ at } T_c^\circ$   
 $P_{\text{O}_2} = \frac{(0.16) (0.131)}{0.370} \text{ or } \frac{n' RT'}{V'} = \frac{0.00079 \times 0.08205 \times 315.4}{0.370}$   
 $= 0.057 \text{ atm} \quad = 0.055 \text{ atm}$
12. Assume  $\Rightarrow P$  after first expansion  $= VP (= p_{\text{NO}_2}) + DP (= p_{\text{O}_2})$  at  $T_3^\circ$
13. Calculate  $\Rightarrow P$  after first expansion at  $T_3^\circ$   
 $\Rightarrow P = 1.58 + 0.06$   
 $= 1.64 \text{ atm}$   
 vs 1.64 measured calculations correct
14. Calculate  $P_{\text{O}_2''}$  in  $V''$  at  $T_3^\circ$  where  $V'' = V_1 + V_2 + V_3$ ,  $T_3^\circ = T''$   
 (No new assumptions)  
 $P_{\text{O}_2''} = \frac{n' RT''}{V''} = \frac{0.00079 \times 0.08205 \times 315.4}{0.606}$   
 $= 0.03 \text{ atm}$
15. Calculate  $\Rightarrow P$  after second expansion at  $T_3^\circ$   
 $\Rightarrow P = 1.58 + 0.03$   
 $= 1.61 \text{ atm}$   
 vs 1.60 atm measured
16.  $\Delta = 0.01 \text{ atm} \equiv 0.1 \text{ psia}$

Figure 31. Equilibrium Pressure Calculations (2 of 2)

A value of 1.60 atm was measured. The agreement is within the accuracy of the measurement and corroborated the rationale. Perfect agreement was found for stock solution 7. Poorest agreement ( $\Delta = 0.11$  atm) was found for stock solution 2, whose vapors were expanded before thermal equilibrium had been established. Excluding this data, it was calculated that decomposition pressure represents approximately 3% of the total pressure measured above Modified HDA in equilibrium with its vapors, at a fixed temperature.

The propellant tank designer must concern himself with the total (equilibrium) pressure exerted by Modified HDA under static conditions. The propellant pump designer must deduct decomposition pressure from the total pressure, to obtain vapor pressure data which apply to the pump inlet under dynamic conditions such that decomposition pressure cannot develop.

## 2.0 TASK 2 - SOLUBILITY TESTS

### 2.1 Corrosion Product Solubility Tests

At constant temperature, a definite amount of a given solute will dissolve in a given solvent. Consider the case of aluminum nitrate ( $\text{Al}(\text{NO}_3)_3$ ) in water. The degree of solution is expressed by the equation:

$$K_{sp} = [\text{Al}^{3+}][\text{NO}_3^-]^3 \text{ at } T_c^\circ \quad (5)$$

where

$K_{sp}$	= Solubility Product, moles/liter
$[\text{Al}^{3+}]$	= Concentration of Aluminum, moles/liter
$[\text{NO}_3^-]$	= Concentration of Nitrate, moles/liter
$T_c^\circ$	= Constant Temperature, $^\circ\text{C}$

The presence of a common ion from another source will reduce the solubility of aluminum nitrate, to preserve the constancy of  $K_{sp}$ .

It can be predicted, therefore, that the solubility of aluminum nitrate will be lower in aqueous nitric acid than in water, because of the contribution of nitrate ions from the acid to the solubility product. The higher the concentration of acid, the lower the solubility of aluminum nitrate. The magnitude of the effect is shown in Table 32. In this table are reported measured values for aluminum in two solvents containing different amounts of nitric acid. As the concentration of nitrate ion from nitric acid was increased, the concentration of soluble aluminum decreased. Also shown are data for cations from a stainless steel. The nitrate of these ions are known to be very soluble in water, but their solubility was drastically reduced in nitric acid solutions.

TABLE 32. MISCELLANEOUS, ROOM TEMPERATURE SOLUBILITY TESTS <sup>a</sup>

Solvent	Corroded	Analysis Supernatant Liquid
35% $\text{HNO}_3$	6061 AA	22,500 ppm (w/w) Aluminum
WFNA	17-7 SS	9 ppm (w/w) Iron
(98% $\text{HNO}_3$ )		14 ppm (w/w) Chromium
		8 ppm (w/w) Nickel
	6061 AA	60 ppm (w/w) Aluminum

<sup>a</sup>Reference 3.

It can also be predicted that the presence of a common cation will reduce the solubility of a given salt. For example, the presence of aluminum fluoride will reduce the solubility of aluminum nitrate, in a given media. The mathematical identity for the effect is given by:

$$S = -\frac{1}{2}x + \sqrt{\frac{1}{4}x^2 + S_0^2} \text{ at } T_c^\circ \quad (6)$$

where

- $S_0$  = Solubility of salt A alone, moles/liter
- $x$  = Concentration of salt B, moles/liter
- $S$  = Solubility of salt A in the presence of salt B, moles/liter
- $T_c^\circ$  = Constant Temperature, °C

When a metal, such as aluminum, is corroded by Standard HDA, aluminum nitrate and aluminum fluoride are formed, in the presence of nitrate and fluoride ions. Each salt reduces the solubility of the other. The picture is further complicated by reductions in solubility due to the presence of the common anions.

Solubility data measured under controlled conditions provide the best basis for predicting when operational problems, such as propulsion system filter plugging, are likely to occur. In Table 33 are summarized data, available at the beginning of this program, concerning the solubility of stainless steel and aluminum corrosion products in HDA, as a function of corrosion inhibitor, and for some specific corrosion products. Also shown are the sources of the solutes. Solubility is expressed in terms of dissolved metal, as determined by atomic absorption analyses. Qualifications about the data are given under comments. In the same columns are given the references from which the data were taken. The comment, Teflon Filter, requires explanation. Such filters may allow particles of solute to pass into the filtrate, causing positive errors in analysis. The table illustrates at a glance the scarcity and semi-quantitative nature of data available at the time.

The use of a stainless steel filter for the solubility tests performed during this program removed much of the uncertainty about the data obtained with a Teflon Filter (Reference 3). A small, predictable increase in iron content for the filtrates was, however, experienced because of the attack of the acid being filtered on the stainless steel pressure filter, and/or films on its interior from previous exposure to acid. The magnitude of this effect was shown in Table 16 and is summarized in Table 34. The latter table also quantifies a larger source of error. To protect the burner of the atomic absorption spectrophotometer from exposure to acid under dynamic conditions, at a relatively high temperature, the analytical procedure employed included a step in which the sample to be analyzed was diluted five-fold with distilled water. Consequently, any error made during analysis was magnified when results were calculated. The relatively poor accuracy for metal concentrations shown in Table 34 reflects these facts. The accuracy of aluminum determinations suffers from added disadvantages. Microscopic particles of alumina may be aspirated into the flame, producing nonhomogeneous conditions, and giving positive errors. The adjustment of flame temperature is extremely critical, and deviations from the optimum temperature will cause an error in results. The foregoing qualifications must be kept in mind when reviewing test data. An alternative to sample dilution, recommended in Reference 8<sup>a</sup>, was rejected on the basis of unsatisfactory experience. The alternative consists of concentrating the metal species by evaporating down the acid, igniting the residue and taking the residue into solution for analysis. The solvent specified was ineffective in totally dissolving residues from even moderately contaminated samples. The immediate result was a tendency to plug the aspirator of the atomic absorption spectrometer. The net result was poor reproducibility of data.

<sup>a</sup>Reference 8. "Military Specification, Propellants, Nitric Acid," MIL-P-7254F, 30 April 1975.

TABLE 33. PRELIMINARY, ROOM TEMPERATURE SOLUBILITY TEST DATA

Source of Solute(s)	Solubility in ppm (w/w)														Comments (Reference)
	HDA						Standard HDA								
	Fe	Cr	Ni	Al	Fe	Al	Fe	Cr	Ni	Al	Fe	Cr	Ni	Al	
CPs -- 321 SS Studies	~230	~25	~25	·	Fe	>Cr	<Ni	·	Fe	>Cr	>Ni	·	In Std. HDA, [F] > [NO <sub>3</sub> ] (9 <sup>a</sup> ). In Mod. HDA, [F-P] > [F] (9).		
CPs -- VAFB SS/AA Equipment	·	·	·	·	>33	>10	>7	>26	·	·	·	·	Acid Unsaturated (10 <sup>b</sup> ).		
CPs -- 0081 AA/347 SS Studies	·	·	·	·	·	·	·	·	·	>15	>5	>11	~37	Small Tanks (2).	
CPs -- BAT SS/AA Equipment	·	·	·	·	>31	>9	>10	~70	·	·	·	·	Teflon Filter (3).		
FeF <sub>3</sub> Reagent	·	·	·	·	~440	·	·	·	·	·	·	·	Teflon Filter (3).		
CrF <sub>3</sub> ·3H <sub>2</sub> O Reagent	·	·	·	·	·	~85	·	·	·	·	·	·	Teflon Filter (3).		
Ni (NO <sub>3</sub> ) <sub>2</sub> ·2H <sub>2</sub> O Reagent	·	·	·	·	·	·	·	·	·	·	·	·	Data Available f T <sup>o</sup> (9).		
NiF <sub>2</sub> Reagent	·	·	·	·	·	·	·	·	~1000	·	·	·	Teflon Filter (3).		
Al (NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O Reagent	·	·	·	~730	·	·	·	·	·	·	·	·	Data Available f T <sup>o</sup> (9).		
AlF <sub>3</sub> ·2H <sub>2</sub> O Reagent	·	·	·	·	·	·	·	·	·	·	·	·	Teflon Filter (3).		

<sup>a</sup>Reference 9. "HDA Corrosion Chemistry," C.C. Addison, N. Logan, Nottingham University, AFRPL-TR-77-85, December 1977.<sup>b</sup>Reference 10. "HDA Analysis," J.D. DeBolt, Lockheed Missiles and Specs Company, VAFB, Unpublished Notes, November 1976.

TABLE 34. ACCURACY OF SOLUBILITY TEST ANALYSES

Type HDA Tested	Type HDA Last Tested	Avg $\Delta$ Fe ppm (w/w)	$\pm$ ppm (w/w)				Comments
			Fe	Cr	Ni	Al	
Modified	Modified	0.5					Attack on Filter Assembly.
	Standard	1.1					Attack on Filter Assembly.
Standard	Standard	1.1					Attack on Filter Assembly.
	Modified	1.1					Attack on Filter Assembly.
Modified			4	3	3	7	After Correcting for Attack on Filter Assembly.

Data from Standard HDA corrosion product solubility tests given in Tables 18 and 20 were rearranged, as Table 35, in a manner which allowed identification of solutions saturated with one or more species at a given temperature. The decision regarding saturation rested on a decrease in concentration of a given metal, after filtration, beyond the limit of accuracy for the analysis of that metal. In the case of iron, for example, the decrease in concentration, reported as the first entry in the table, signified that one or more species of iron had reached saturation at 75°F (24°C), at a level of 20 ppm. No significant differences were found when temperature was reduced to 42°F (5.6°C), when H<sub>2</sub>O content was raised from 0.7 to 1.0, and finally to 1.7 wt%, and when NO<sub>2</sub> content was increased from 34 to 43 wt%. Further inspection of the table reveals that one or more chromium species precipitated when H<sub>2</sub>O and NO<sub>2</sub> were raised to the highest level studied. It will be noted that chromium and iron concentrations were indistinguishable in the solution saturated with both metals. As was found for iron, no significant difference was noted when temperature was reduced to 42°F (5.6°C). None of the solutions proved to be saturated with nickel, under the conditions tested. By contrast, all the solutions tested were saturated with one or more species of aluminum. This conclusion was reinforced by the large amounts of particulate matter measured as part of the solubility test procedure. Deductions concerning the effects of increased H<sub>2</sub>O content or decreased temperature at low NO<sub>2</sub> content must be qualified because atomic absorption results fall within the limits of the methods. Deductions for results at higher NO<sub>2</sub> content must be guarded because of uncertainty in the efficiency of the filtration procedure employed. What is certain is the fact that whereas some species of aluminum had exceeded their solubility limit(s), at least one other species has a solubility limit above 35 ppm.

Combining data from particulate analyses with the principles of solubility leads to the conclusion that the Standard HDA solutions studied contained a mixture of corrosion products from natural attack on aluminum alloys and stainless steels. In addition to fluorides and nitrates, oxides will be present by natural transformations of nitrates formed in the vapor phase. The oxides are known to be very insoluble, and their solubility limits will easily be exceeded. Most of the particulate matter collected during filtration was an oxide of aluminum. The relatively high concentrations of metals in solution are attributed to the solubility of their fluorides and nitrates, principally their nitrates. The practical conclusions drawn from these tests are that provisions must be made to reduce vapor phase exposure of metal to acid fumes to a minimum, and to provide filters for removing oxides which do form and precipitate. A filter with a pore size of 5 $\mu$  (micron) appears adequate for the task. Addition

TABLE 35. STANDARD HDA CORROSION PRODUCT SOLUBILITY TESTS

Species	at T°		at NO <sub>2</sub> wt %	at H <sub>2</sub> O wt %	Pre Range, ppm	Post Range, ppm	Saturated Solution?	Reference
	°F	°C						
Iron	75	24	34	0.7	35	24	Yes, Some Species	Table 18, Test No. 8.
	68	20	34	0.7	36-41	24-28	Yes, Some Species	Table 18, Test Nos. 11-14.
	75	24	34	1.0	38-42	25-28	Yes, Some Species	Table 18, Test Nos. 9-10.
	72	22	43	1.7	98	20	Yes, Some Species	Table 20, Test No. 1.
	42	5	43	1.7	93	26-28	Yes, Some Species	Table 20, Test Nos. 5-6.
Chromium	75	24	34	0.7	10	10	No	Table 18, Test No. 8.
	68	20	34	0.7	11-12	10-12	No	Table 18, Test Nos. 11-14.
	75	24	34	1.0	11-14	10-13	No	Table 18, Test Nos. 9-10.
	72	22	43	1.7	34	25	Yes	Table 20, Test No. 1.
	42	5	43	1.7	34	26-28	Yes	Table 20, Test Nos. 5-6.
Nickel	75	24	34	0.7	11	11	No	Table 18, Test No. 8.
	68	20	34	0.7	11-12	11-12	No	Table 18, Test Nos. 11-14.
	75	24	34	1.0	13-14	10-13	No	Table 18, Test Nos. 9-10.
	72	22	43	1.7	36	34	No	Table 20, Test No. 1.
	42	5	43	1.7	36	34-37	No	Table 20, Test Nos. 5-6.
Aluminum	75	24	34	0.7	52	35	Yes, Some Species	Table 18, Test No. 8.
	68	20	34	0.7	36-41	46-49	Yes, Some Species	Table 18, Test Nos. 11-14.
	75	24	34	1.0	63-75	50-62	Yes, Some Species	Table 18, Test Nos. 9-10.
	72	22	45	0.6	~78	~70	Yes, Some Species	Reference 3.
	25	-4	45	0.6	~78	~80	Yes, Some Species	Reference 3.



of  $H_2O$  to the system should be avoided, to reduce the likelihood of forming hydrated oxides, which tend to be gelatinous, and difficult to remove without frequent changes of filters. With oxide problems under control, one can expect to approach metal concentrations in excess of 20 ppm, without precipitation, over normal operating temperature ranges.

An evaluation parallel to that just described for Standard HDA was performed for the first series of solubility tests of corrosion products formed by interaction of Modified HDA and stainless steel and aluminum alloys. These tests involved solutions containing relatively low concentrations of corrosion products. The results of the evaluation are shown in Table 36. It is apparent that the original stock solution was not saturated with stainless steel corrosion products at room temperature. Furthermore, saturation was not induced by increases in  $H_2O$  or  $NO_2$  contents, or by a decrease in temperature, over the ranges studied. As was the case with Standard HDA, isolation of particulate matter and consideration of the principles of solubility led to the conclusion that the solubility of aluminum oxide had been exceeded when the aluminum content of the acid exceeded 5 ppm. Changes in  $H_2O$  and  $NO_2$  contents, and temperature did not affect this limit.

Evaluation of data along the lines described for solubility tests at the lowest concentrations studied of stainless steel corrosion products in Modified HDA (Series 1) was carried out for solutions containing higher concentrations. The results of the evaluation are given in Table 37. With one exception, the solutions as-received were unsaturated, and increases in  $H_2O$  (to 1.0 wt %) and  $NO_2$  contents, and decreases in temperature, over the range studied, did not induce precipitation. When, however,  $H_2O$  content was increased to 1.7 wt%, precipitation of an iron species was induced. This is another argument in favor of restricting the  $H_2O$  content of HDA. The net effect of these tests was to raise the measured levels of soluble iron, chromium and nickel containing corrosion products in Modified HDA above the levels studied in Test Series 1. Furthermore, it was demonstrated that the solubility levels of iron containing species are similar in Modified HDA and Standard HDA.

Acid analyses for the concentration of aluminum from corrosion products in Modified HDA, at the highest levels considered during this program, are summarized in Table 38. These analyses indicate that some species of aluminum are soluble at levels in excess of 35 ppm. The rationale applied to explain the range in solubility limits noted for Standard HDA applies equally well to Modified HDA. A low solubility is attributed to the pressure of an oxide. It is precisely the same compound,  $Al_2O_3$  (aluminum oxide) described as first precipitating from Standard HDA. Higher solubilities are possessed by the nitrates, fluorides and fluorophosphates of aluminum. The last named species is associated only with Modified HDA. It is present because of the use of  $PF_5$  as the corrosion inhibitor. This inhibitor is thought to give rise (Reference 9) to difluorophosphates and hexafluorophosphates, not only of aluminum, but also of iron, chromium and nickel, when corrosion of stainless steel as well as aluminum alloy is involved. Because the same, relatively insoluble species,  $Al_2O_3$ , may be encountered in Modified HDA and Standard HDA, the precautions cited in reference to handling Standard HDA should be applied to Modified HDA. More soluble aluminum species, posing fewer problems, are also associated with both oxidizers. Data currently available suggests that the solubility levels of aluminum containing species present in Standard HDA are above the levels for the species present in Modified HDA. This matter will presently receive further consideration.

Table 38 also contains the results of particulate analyses made as part of solubility tests with Modified HDA blends containing high concentrations of aluminum and stainless steel corrosion products. Even allowing for the semiquantative nature of the data, it is apparent that an increase in water content or a decrease in temperature may result in an increase in particulate matter. The data are challenged by the failure of atomic absorption analyses to reveal corresponding decreases in the metal contents of the filtrates.

TABLE 36. MODIFIED HDA CORROSION PRODUCT SOLUBILITY TESTS - SERIES I

Species	at T°		at NO <sub>2</sub> wt %	at H <sub>2</sub> O wt %	Pre ppm	Post ppm	Solution Saturated?	Effect			Reference	
	° F	° C						Δ NO <sub>2</sub>	Δ H <sub>2</sub> O	Δ T°	Table No.	Test No.
Iron	72	22	43	0.3	8	7	No	None	None	None	19	1
					6	6	No	None	None	None		4
					11	12	No	None	None	None		7
Chromium	72	22	43	0.3	2	2	No	None	None	None	19	1
					2	3	No	None	None	None		4
					2	2	No	None	None	None		7
Nickel	72	22	43	0.3	3	3	No	None	None	None	19	1
					3	4	No	None	None	None		4
					3	3	No	None	None	None		7
Aluminum	72	22	43	0.3	8	5	Yes, See Particulate	None	None	None	19	1
					9	7	Yes, See Particulate	None	None	None		4
					6	4	Yes, See Particulate	None	None	None		7
Particulate	72	22	43	0.3	.	20	Yes, Some Species	None	None	None	19	1
					.	20	Yes, Some Species	None	None	None		4
					.	33	Yes, Some Species	None	None	None		7

TABLE 37. MODIFIED HDA CORROSION PRODUCT SOLUBILITY TESTS - SERIES 2 AND 3

Species	at T°		at NO <sub>2</sub> wt%	at H <sub>2</sub> O wt%	Pre ppm	Post ppm	Solution Saturated?	Effect			Reference
	° F	° C						Δ NO <sub>2</sub>	Δ H <sub>2</sub> O	Δ T°	
Iron	72	22	43	0.5	22	21	No	None	None	None	Table 20, Test No. 2.
	~77	~25	45	0.3	15	15	No	.	.	.	Reference 2, SS Tank No. 3.
	72	22	43	1.0	45	38	No	.	.	None	Table 21, Test No. 1.
	42	5	43	1.0	45	38	No	.	.	.	Table 21, Test No. 2.
	40	5	43	1.7	38	26	Yes	.	Less Soluble	.	Table 21, Test No. 3.
Chromium	72	22	43	0.5	6	6	No	None	None	None	Table 20, Test No. 2.
	~77	~25	45	0.3	6	6	No	.	.	.	Reference 2, SS Tank No. 3.
	72	22	43	1.0	8	6	No	.	None	None	Table 21, Test No. 1.
	72	22	43	0.5	5	5	No	None	None	None	Table 20, Test No. 2.
Nickel	~77	~25	45	0.3	10	11	No	.	.	.	Reference 2, SS Tank No. 3.
	72	22	43	1.0	8	8	No	.	None	None	Table 21, Test No. 1.

TABLE 38. MODIFIED HDA CORROSION PRODUCT SOLUBILITY TESTS - SERIES 3

Species	at T°		at NO <sub>2</sub> wt %	at H <sub>2</sub> O wt %	Pre ppm	Post ppm	Solution Saturated?	Effect			References
	°F	°C						Δ NO <sub>2</sub>	Δ H <sub>2</sub> O	Δ T°	
Aluminum	72	22	43	1.0	31	28	No	-	None	None	Table 21, Test No. 1.
	~77	~25	44	0.3	42	35	Yes, Some Species	-	-	-	Reference 2, AA Tank No. 3.
Particulate	72	22	43	1.0	-	114	-	-	-	-	Table 21, Test No. 1.
	42	5	43	1.0	-	130	-	-	-	Increases	Table 21, Test No. 2.
	40	5	43	1.7	-	141	-	-	Increases	-	Table 21, Test No. 3.

The time required for the first appearance of particles of corrosion products in HDA is the time required to satisfy the solubility product of a particular species. The time is variable, because under different conditions of storage, different species can form. The most apparent variables for a given type of HDA and a given type of storage vessel are the ullage space and S/V ratio. Data presented in Figure 32 bring out these relationships.

Figure 32 contains plots of aluminum content found for aliquots of several samples of Modified HDA, taken as a function of time. A solid line signifies that the corresponding aliquots were clear. The line is broken to represent the presence of visible particles of corrosion products. The tests of longest duration involved three, small, aluminum tanks, sampled at regular intervals over a period of three years. Each year one tank was removed from test. The first tank removed, S/N-1, exhibited clear samples and a gradual rise in aluminum content to 8 ppm, in one year. On disassembly and inspection, the tank interior was found to be free of corrosion products. Particles were observed in aliquots taken from tank S/N-2, from the seventeenth month, to the end of the second year. A mixture of aluminum corrosion products was found in the tank during post test inspections. Aluminum content of the acid had exceeded 20 ppm before particles were observed. At this point, it appears that the solubility product of aluminum oxide was exceeded. From the identity of the layers of corrosion products found in the tank, post test, it appears that the next salt to precipitate was  $\text{AlPO}_4$  (aluminum phosphate). A similar pattern was noted for tank S/N-3. The somewhat longer time required for particles to appear (20 months) is attributed to the fact that sampling was done less frequently, to conserve the acid in tank S/N-3 for the maximum test duration. Therefore, at any given time, the ullage space was less, and the S/V ratio was smaller, for tank S/N-3 than for tank S/N-2. These are preferred conditions for long term storage. Other tests depicted in Table 34 involved a metal sampler, from which aliquots of Modified HDA were drawn for one test ( $S_1$ ), and are being drawn for another ( $S_2$ ). All samples drawn to date have appeared clear. A relatively high aluminum content was found by the end of a relatively short test, represented by  $S_1$ . The sampler had been pickled with aqueous acids before test, and was stored relatively full. The rapid increase in aluminum content in aliquots drawn for analysis is attributed largely to solution of soluble salts related to the pickling operations. The clarity of the acid is attributed to the fact that insufficient time was allowed for formation of noticeable amounts of  $\text{Al}_2\text{O}_3$ . A small crop of white crystals was however, isolated by filtration of the acid, post test. Electron microprobe (emp) analyses were positive for aluminum, oxygen and phosphorous. This is consistent with the postulated presence of  $\text{Al}_2\text{O}_3$  and  $\text{AlPO}_4$ . The sampler was refilled and is exhibiting a lower rate of formation of soluble aluminum salts ( $S_2$ ). The acid in the sampler, and in companion aluminum test vessels (V), are being reserved for future tests. It is already clear that dedication of a storage tank to one type of acid is preferred, as are storage at low ullage and low S/V ratio, if extended storage, free of troublesome particulate matter is desired.

The benefits of dedicating a tank to service with a particular acid are further demonstrated by data in Table 39. The data in this table also test the hypotheses (Reference 9) that corrosion rate of metals exposed to HDA, are controlled by the concentration of corrosion products in the acid, rather than by establishment of a protective film. Page one of Table 39 contains the results from a test in which a segment of aluminum tank S/N-3 (Reference 2), with a granular deposit on one surface, was immersed in a clear, Kel-F bottle of pure, Modified HDA. The specimen was examined visually, without removing it from the acid, at regular intervals, over a period of two months. On four occasions, aliquots of acid were withdrawn for determinations of aluminum content. No changes in the appearance of the specimen or acid were noted during the test. Admittedly, the deep, red color of the acid tended to mask changes in appearance of the specimen or the appearance of particles in the acid, but gross changes would not have been overlooked. The qualifications concerning detection of particles in the acid apply to all cases for which the physical appearance of HDA is re-

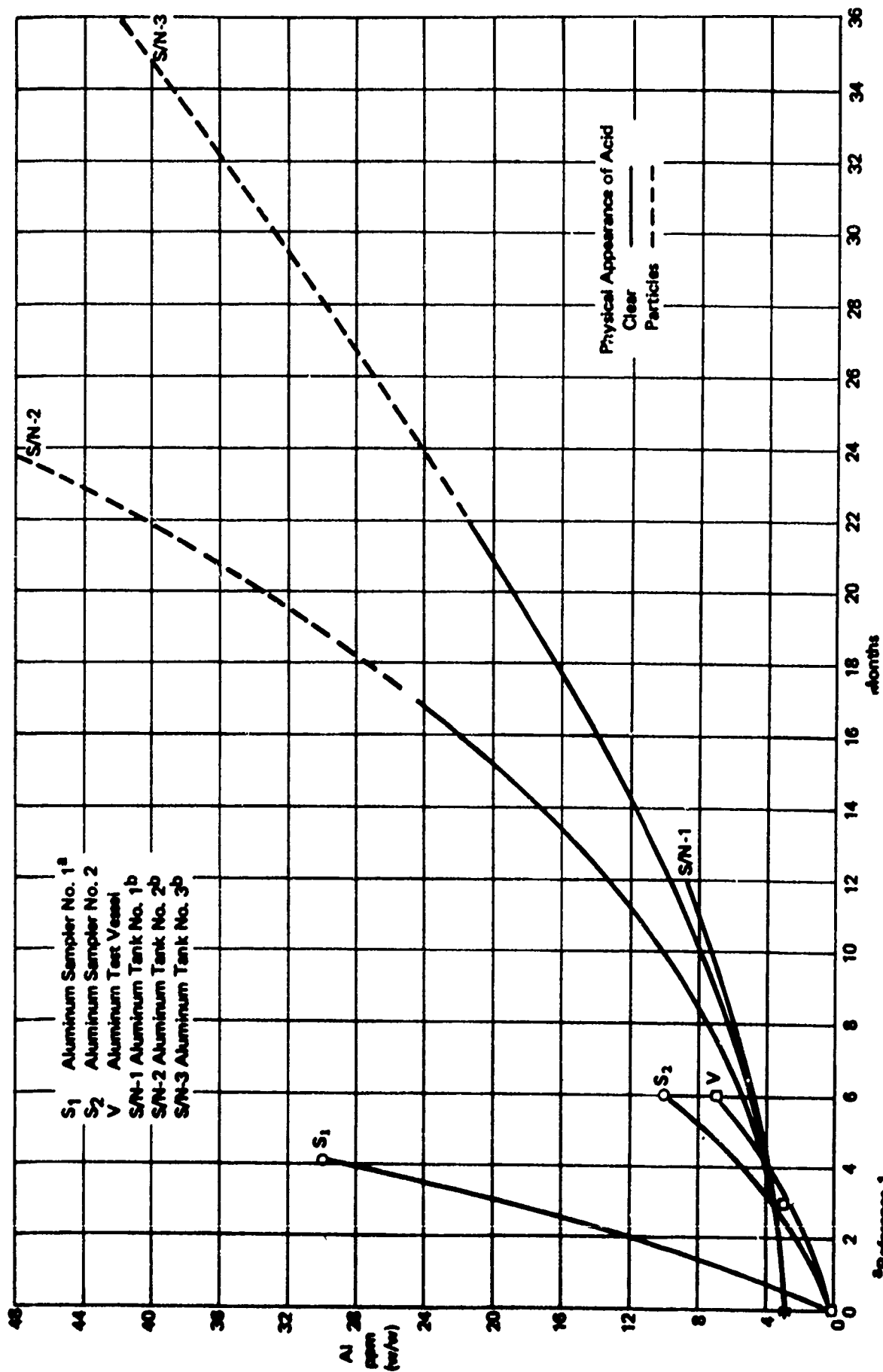


Figure 32. Solubility of Aluminum Salts in Modified HDA

<sup>a</sup>Reference 1.  
<sup>b</sup>Reference 2.

ported. The conclusions drawn were confirmed, moreover, by the fact that no significant change was found for the granular deposit on one side of the specimen. The slight increase in aluminum content of the acid was attributed to attack on the other side of the specimen. Such results strengthen the argument that formation of a protective film impedes corrosion of aluminum by Modified HDA. The results also argue in favor of dedicating a tank to a particular type of acid service.

The results for a parallel test with a segment of a companion, stainless steel tank (Reference 2) are given on the second page of Table 39. No changes in the appearance of the specimen or the acid were detected by visual examination, but within two weeks a marked increase in the iron content of the acid was measured. The sample was accordingly removed from test. A change in the appearance of the surface was then apparent. A tightly adherent green film had been transformed into a loose, granular, white salt. Analyses by emp related these changes to solution of chromium and nickel species in the original film. Although such results weaken the argument for corrosion inhibition by film formation, and dedication of a tank to a particular type of acid service, the results of the long duration tests described in Reference 2 suggest that damage to the film would be repaired and corrosion impeded by the film, before the acid was saturated with corrosion products. Further tests would be necessary to settle the matter unequivocally. Until such time, the conclusions first drawn are endorsed.

TABLE 39. SOLUBILITY OF CORROSION PRODUCT FILMS (1 of 2)

Test Parameters						
Test Specimen	Solvent	Temp		Test Duration Days	S/V in <sup>-1</sup>	Comments
		°F	°C			
6061 AA - CPs	Pure, Mod. HDA	70	21	63	1.0	Liquid Phase Exposure.
Test Results						
Appearance of Metal						
Pre Test	Tightly adherent, thin, black band, adjacent to white, granular deposit.					
Post Test	Granular deposits swelled during test, reverted to original appearance after washing and drying.					
Acid Analyses						
		Days in Test	Physical Appearance	Al ppm (w/w)		
		0	Clear	1.0		
		12	Clear	1.0		
		21	Clear	3.0		
		63	Clear	4.0		

TABLE 39. SOLUBILITY OF CORROSION PRODUCT FILMS (2 of 2)

Test Parameters								
Test Specimen	Solvent	Temp.		Test Duration Days	S/V in <sup>-1</sup>	Comments		
		°F	°C					
347 SS - CPs	Pure, Mod. HDA	70	21	14	1.0	Liquid phase exposure.		
Test Results								
Appearance of Metal								
Pre Test	Tightly adherent, thin, green film.							
Post Test	Loose, granular, white salt.							
Corrosion Product Analyses								
		Fe	Cr	Ni	P	F	N	O
Pre Test - Top Layer - Green		+	+	+	+	+	+	+
Post Test - Top Layer - White		+	-	-	?	-	-	-
- Lower Layer - Green		+	?	-	+	-	-	-
Acid Analyses								
		ppm (w/w)						
	Days In Test	Physical Appearance	Fe	Cr	Ni			
	0	Clear	4	<1	1			
	7	Clear	12	1	1			
	14	Clear	14	1	1			

One final set of solubility tests was performed during this program with readily available samples of aluminum species expected to be found among the corrosion products in Modified HDA. These tests involved saturation of separate portions of pure, Modified HDA with reagent grade aluminum oxide, aluminum fluoride and aluminum phosphate. The aluminum compounds were heated before test to 212°F (100°C), to dry the oxide, to dehydrate the fluoride, and to reduce the phosphate to the dihydrate. The fluoride as-received was a dihydrate, the phosphate was a tetrahydrate. Water was removed to transform the compounds as closely as possible to the forms in which they most likely exist in Modified HDA. An earlier test (Reference 3) with Standard HDA was conducted with aluminum fluoride as-received. The results of these tests are included in Table 40. The difference between the solubility of aluminum fluoride in Modified HDA and in Standard HDA appears to be greater than could be attributed to the degree of hydration of the starting compounds. Aluminum fluoride is probably more soluble in Modified HDA than in Standard HDA. The still higher solubility of the dihydrate of aluminum phosphate is also open to question. Tests with the anhydrous salt could



TABLE 40. CURRENT, ROOM TEMPERATURE SOLUBILITY TEST DATA

Source of Solute(s)	Solubility in ppm (w/w)													
	HDA						Standard HDA						Modified HDA	
	Fe	Cr	Ni	Al	Fe	Al	Fe	Cr	Ni	Al	Fe	Cr	Fe	Al
CPs - 321 SS Studies	~230	~25	~25		Fe	>Cr	Fe	>Cr	<Ni		Fe	>Cr	~Ni	See Table 21 (9)
CPs - VAFB SS/AA Equipment					>33	>10			>7	>26				Acid Un-saturated (10).
CPs - 6061 AA/347 SS Studies											>15	>5	11 ~37	Small Tanks (2)
CPs - BAT SS/AA Equipment					20-28	25-28	>37	~35-70	>37	~35-70	>21	>6	~11 4-35	Pressure Filter (This Work).
FeF <sub>3</sub> Reagent					~440									Teflon Filter (3)
CrF <sub>3</sub> · 3 H <sub>2</sub> O Reagent						~85								Teflon Filter (3)
Ni (NO <sub>3</sub> ) <sub>2</sub> · 2 H <sub>2</sub> O Reagent			~4700											See Table 21 (9)
Ni F <sub>2</sub> Reagent									~1000					Teflon Filter (3)
Al (NO <sub>3</sub> ) <sub>3</sub> · 6 H <sub>2</sub> O Reagent			~730											See Table 21 (9)
Al F <sub>3</sub> · 2 H <sub>2</sub> O Reagent										~6				Teflon Filter (3)
Al F <sub>3</sub> Reagent														Pressure Filter (This Work).
Al <sub>2</sub> O <sub>3</sub> Reagent														Pressure Filter (This Work).
Al PO <sub>4</sub> · 2 H <sub>2</sub> O Reagent														Pressure Filter (This Work).

easily prove it to be less soluble than the anhydrous fluoride. This would match the order suggested in Reference 2. Even more pertinent would be tests with the difluorophosphate and hexafluorophosphate of aluminum (Reference 9). Attempts to date to locate a commercial source of these salts have been unsuccessful.

Also shown in Table 40 are corrosion product solubility data updated from Table 33. The changes relate to entries concerning the solubility of aluminum and stainless steel corrosion products in Standard HDA and Modified HDA. This program has better defined the limits of solubility for the species and acids involved. With reference to Standard HDA at room temperature, precipitation of stainless steel corrosion products can be expected when iron (or chromium) content exceeds 20-28 ppm. If allowed to form,  $\text{Al}_2\text{O}_3$  may appear in particulate form at low levels of aluminum. Under normal circumstances precipitation of aluminum corrosion products can be expected when aluminum content exceeds 35-70 ppm. For large tanks of acid, higher concentrations of aluminum (or stainless steel elements) can be expected at any given time at the walls than in the center of the liquid. The diffusion of corrosion products formed at the walls throughout the liquid is thought to be a slow process. Once corrosion product precipitation occurs (near the walls), the products will tend to settle to the bottom of the tank. For these reasons, obtaining a representative sample from a large tank becomes increasingly difficult. Less definitive data are available concerning the limits of solubility of stainless steel corrosion products in Modified HDA. It now appears, however, that the levels may be similar to those in Standard HDA. The upper limits for the solubility of aluminum corrosion products in Modified HDA also require better definition. At present it appears that they may be lower than the levels in Standard HDA. Comments made concerning large tanks of Standard HDA apply equally well to Modified HDA.

Stocks of Standard HDA containing naturally occurring stainless steel and aluminum corrosion products are available for further studies, especially of the effects of changes in  $\text{H}_2\text{O}$  and  $\text{NO}_2$  contents, and changes in temperature. Tests solutions are being prepared for exploring the effects of higher aluminum contents from corrosion of an aluminum alloy by Modified HDA. Synthesis of the fluorophosphates of aluminum is being considered to resolve another open facet of Modified HDA studies. The remaining open facet would involve corresponding studies with higher concentrations of stainless steel corrosion products and the fluorophosphates of iron, chromium and nickel.

## 2.2 Passivation Tests

One of the hypotheses advanced to explain the decrease in corrosion rate with time noted for metals exposed to a given type of HDA rests upon the existence of films of corrosion products found in tanks after extended exposure to Modified HDA (Reference 2). Films such as these may act as a barrier to further attack of the underlying metal by the HDA. Another hypothesis (Reference 9) rests upon the observed changes in rate of corrosion product buildup in solution. After a time, no further increase in metal content is found. This is related to saturation of the HDA with corrosion products, and inhibition of further corrosion. The difference between the hypotheses is that corrosion may be impeded by a film before the HDA is saturated with corrosion products, in one case; no film formation is required to impede corrosion in the other. The hypotheses are in agreement about three steps being involved to reach a passive state, i.e., one in which no further corrosion occurs. An initial attack must occur to convert the surface of a metal to a form unique to a HDA environment. This step may be likened to a cleaning or pickling reaction in which the film present from exposure to the previous media is removed. The fresh surface then undergoes rapid attack, at a constant rate (the corrosion rate of the given metal in the given HDA, at a given temperature). After a time, where film formation, or solution saturation occurs, the corrosion rate falls off. The system may now be considered passive.

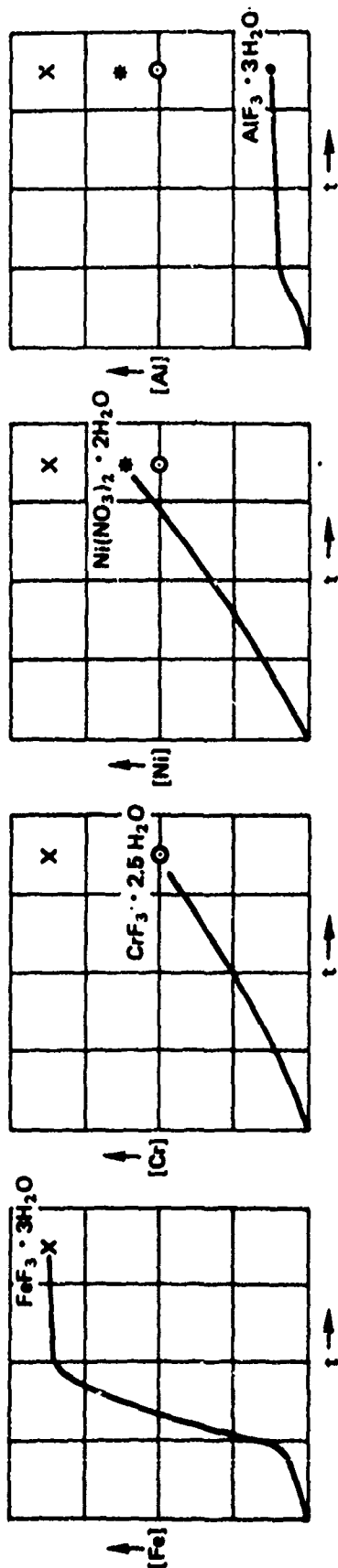
From an operational standpoint, it would be ideal if passivation took place quickly, and disposed the metal so that the acid used for passivation could be replaced with pure acid. The time until its contamination with corrosion products would then be extended indefinitely. A number of tests have been conducted to evaluate this possibility.

The passivation tests involved the metals in the Agena oxidizer tank sump, because the design of the sump is such as to create a high S/V ratio when the sump is full of acid. According to Reference 9, such a ratio should be associated with rapid saturation of the acid with corrosion products, and an early decrease in corrosion rate. On this basis, over an extended period of time, a lower, average corrosion rate will be associated with a system with a high S/V ratio than with a system containing a low S/V ratio. The inference is a preference for a system with a high S/V ratio. The penalties one can expect with a high S/V ratio system, however, are the early appearance of particles of corrosion products, and filter plugging in propulsion systems. These penalties derive as the acid becomes contaminated, and the metal becomes disfigured. Corrosion rates, based on the hypothesis of film formation, measurements in terms of weight change of the metal, and appearance of corrosion products in the acid, also reflect these penalties, and immediately rank a high S/V ratio system as more deleterious than one with a low S/V ratio. The frame of reference, therefore, appears to set up contradictions not only in the mechanism of passivation, but also in the effect of S/V ratio. There is, in fact, no disagreement about the practical effects of a given S/V ratio.

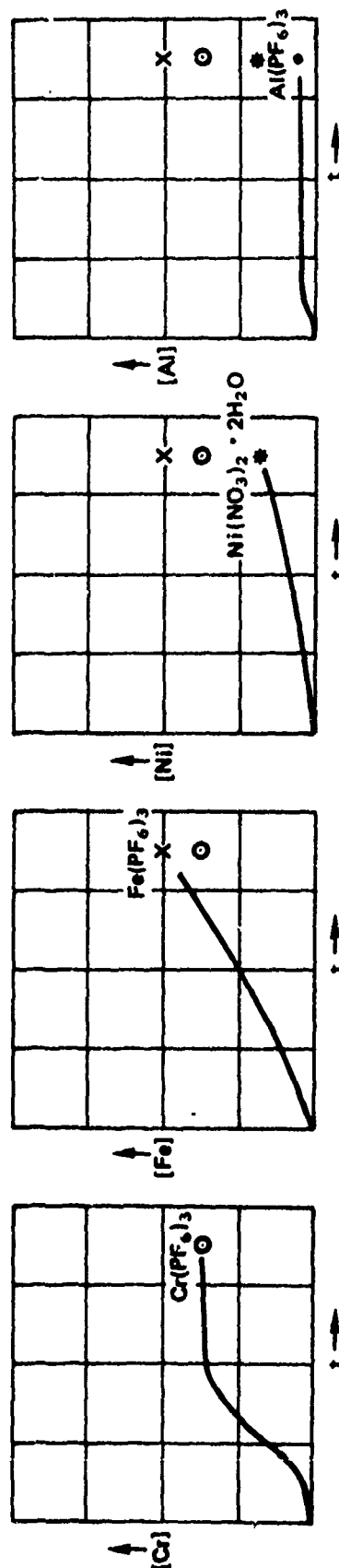
Before examining the results of specific passivation tests, attention is directed to Figure 33. In this figure are curves depicting the passivation of stainless steel and aluminum alloys exposed to Standard HDA or Modified HDA. The curves were drawn from data in Reference 9. They show, in a semiquantitative way, the buildup of iron, chromium, nickel and aluminum (Fe, Cr, Ni and Al) in acid, as a function of time. Constant temperature is implied. The curves for Standard HDA indicate control over corrosion of stainless steel by saturation of the acid with a relatively large amount of the trihydrate of ferric fluoride,  $\text{FeI}_3 \cdot 3\text{H}_2\text{O}$ . When the acid is saturated with this salt, corrosion is arrested. At this point, a smaller concentration of the dihydrate of nickel nitrate,  $\text{Ni}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ , and a still smaller concentration of a hydrated chrome fluoride,  $\text{CrF}_3 \cdot 2.5\text{H}_2\text{O}$  exist in the acid. Corrosion of aluminum alloys is accompanied by saturation of Standard HDA with a relatively small amount of the trihydrate of aluminum fluoride  $\text{AlI}_3 \cdot 3\text{H}_2\text{O}$ . In the case of Modified HDA, stainless steel corrosion is controlled by saturation of the acid with a fluorophosphate of chromium, e.g.,  $\text{Cr}(\text{PF}_6)_3$ . Modified HDA is less corrosive to stainless steel and aluminum alloys so the concentration of chromium from  $\text{Cr}(\text{PF}_6)_3$  in Modified HDA, at the point of passivation, is less than the concentration of iron in Standard HDA. Because of the ratios of Fe, Cr, and Ni in stainless steel, the concentration of iron in Modified HDA at the passivation point will exceed that of chromium, but the solution will not be saturated with the iron salt. The solution will likewise be unsaturated with a nickel salt. The salt will be the nitrate, at relatively low concentration. The corrosion of aluminum will be arrested by saturation of Modified HDA with a relatively small amount of a fluorophosphate, such as  $\text{Al}(\text{PF}_6)_3$ . Reference 9 indicates that true passivation of stainless steel in Standard HDA will require more than 30 days. Passivation in Modified HDA can be expected in approximately one day. Less definitive data were reported for aluminum alloys.

The first test of the foregoing predictions was provided by the data in Table 41. These data, from Reference 1, pertain to tests of couples of stainless steel cloth and aluminum alloy sheet stock, simulating the couples in the sump of the Agena oxidizer tank. The couples contained a larger area of aluminum than stainless steel (1.4/1.1), but the ratio was less than that in the sump (4/1). The amount of acid used for each test was sufficient to give a S/V ratio of  $1.0 \text{ in}^{-1}$ , in terms of stainless steel. The corresponding ratio in the sump is  $2.0 \text{ in}^{-1}$ . These variations will presently receive further consideration. The tests summarized in Table 41 included separate measurements with Standard HDA and Modified HDA. All of the tests were conducted at the same temperature. Test durations were: 30, 60, 90 and 150 days. A slow, gradual attack was noted on the couples exposed to Modified HDA. Between 90-150

# Standard HDA



# Modified HDA



Reference 8

Figure 33. Prediction of Passivation Test Results

**Material** 304 SS Cloth/6061-O.W.

**Reference 1.**

<sup>b</sup> Refer to Table 31 for Rating Scheme.

<sup>c</sup>Salts trapped in specimens

days, a tan film appeared on the aluminum. The acid appeared to be free of particles. Corrosion rate, as determined by weight changes, was very low. Fe content had risen to 17 ppm, compared with 3 ppm of Cr and Ni and 2 ppm of Al.

Within 30 days, the bare aluminum alloy exposed to Standard HDA was covered with a black film. There were white corrosion products on the stainless steel cloth. Particles were visible in the acid, and iron content had risen to 21 ppm. Although the acid was saturated with some species of metals, corrosion proceeded, as evidenced by further loss of weight of the test specimens, and deterioration of acid quality. At the end of 120 days, the concentrations of Fe, Cr, Ni and Al in the acid were 80, 118, 148 and 1 ppm, respectively. In defense of Figure 33, it should be noted that the relative concentrations of Fe, Cr, Ni and Al in Standard HDA and Modified HDA were precisely as predicted.

The scheme for rating corrosion experiments of the type included in Table 41 is covered in Table 42. Both the effect of the propellant on the metal, in terms of corrosion rate, measured by weight change of the metal, and the effect of the metal on the propellant, in terms of propellant purity, as measured by analyses, are considered. When a low corrosion rate and high propellant quality are found, a rating of 1 is applied. This signifies a capacity for excellent service, over an extended period of time, under the conditions tested. Use is restricted when either criteria fails to be met satisfactorily. A rating of 2 restricts a given metal/propellant combination to repeated, short term usage. A rating of 3 reduces service to single, short term usage. It is not recommended that combinations with a rating of 4 be used. Without exception, better ratings were exhibited by Modified HDA than for Standard HDA, for the tests summarized in Table 40.

TABLE 42. COMPATIBILITY CLASSIFICATION OF MATERIALS WITH ROCKET PROPELLANTS

Compatibility Classification of Metals				
Class	1	2	3	4
Rating	Excellent	Good	Fair	Poor
Corrosion Rate in Mils/Year	1	<5	5 to 50	>50
Decomposition of Propellant	No	No	Some	Extensive
Compatibility Classification of Nonmetals				
Class	1	2	3	4
Volume Change in Percent	0 to +25	-10 to +25	-10 to +25	< -10 or >+25
Durometer Reading	±3	±10	±10	< -10 or >+10
Effect on Propellant	None	Slight Change	Moderate Change	Severe
Visual Examination	No Change	Slight Change	Moderate Change	Severely blistered, cracked, or dissolved
General Usage	Satisfactory For General Use	Satisfactory For Repeated Short-Term Use	Satisfactory For Short-Term Use	Unsatisfactory

Results of tests reported in Reference 7 to obtain additional data on the passivation of couples of the type in the Agena oxidizer sump tank, during exposure to Standard HDA for periods up to 48 hours, are summarized in Table 43. These tests were more realistic, in that the area ratio of the aluminum alloy and stainless steel in the sump (4/1), was used for the tests. The S/V ratio was not duplicated. A value of  $0.3 \text{ in}^{-1}$ , in terms of stainless steel, was employed. In addition to couples of the more prevalent type in the sump, those containing stainless steel cloth, a couple containing stainless steel screen was also tested. For convenience, 6061 AA was used in the form of tubing, to complete the couples. Specimens of each type of metal were tested separately (uncoupled) for 48 hours, as "blanks". Between 24 and 48 hours, attack on the stainless steel cloth containing couples become evident. The acid appeared clear, but the metals exhibited films. Analyses of the acids revealed increases of 3 ppm and 1 ppm for Fe and Cr, respectively. There were no measurable increases in Ni or Al contents. Film formation was occurring before saturation of the acid sample with corrosion products. The "blanks" exhibited no sign of film formation, indicating that coupling was deleterious. The same conclusion was suggested by the slightly lower concentration of Fe in the acid for the stainless steel cloth "blank". Since the results for metals in all of the acids discussed to this point were near the limits of the accuracy of the method, the conclusions drawn must be qualified. The tests with stainless steel screen clearly indicate, however, that more attack will occur in a given time with couples containing stainless steel screen, than with couples containing stainless steel cloth. In summary, this series of tests indicated that film formation began in Standard HDA before the acid was saturated with corrosion products. Passivation was not evident within two days.

The most realistic passivation tests to date were those performed as part of this program. These tests included couples of both types found in the Agena oxidizer sump, along with "blanks". Couples were tested with the same area ratio (4/1) of aluminum alloy and stainless steel found in the sump. The S/V ratios chosen matched those for the stainless steel cloth and aluminum alloy (6061-T4) in the sump, viz.,  $2.0 \text{ in}^{-1}$  for the stainless steels and  $8.0 \text{ in}^{-1}$  for the aluminum alloys. A full complement of tests was run with 6061-T4 AA/304 SS Cloth couples in Modified HDA. A set of couples including 6061-T6 AA and 347 SS Screen, and "blanks", rounded out the Modified HDA test matrix. A representative number of tests was run with Standard HDA, in order to obtain data for comparing the two oxidizers. The test details were described fully in Section II. Also presented were tables, plots of test data, and some discussion of the test results. The discussion continues with reference to Figure 34.

Figure 34 contains sample calculations for the weight change of the couple used for test No. 1, and for the corrosion rates for the components of the couple. The results of the calculations also appear in Table 25 and Figures 20, 21 and 22, along with data for the other tests. It was expected that deposits of corrosion products would form during these tests, as they had during the tests described in Reference 1. An increase in weight would be a direct measure of deposit formation. For the case chosen, a weight increase of 1.8 mg was found. This is well within the accuracy of the method ( $\pm 0.2 \text{ mg}$ ). However, the presence of corrosion products was not apparent. It was concluded, therefore, that film formation accounted for the weight change. The location of the film was detected by corrosion rate calculations in Figure 34. For the case chosen, a weight loss was found after the aluminum portion of the couple was cleaned and reweighed. This weight loss corresponded to a corrosion rate of  $0.0006 \text{ mg/cm}^2/0.25 \text{ hour}$ . This value lies at the limit of accuracy of the method ( $\pm 0.0006 \text{ mg/cm}^2$ ), and must be judged accordingly. Parallel calculations for the stainless steel component of the couple indicated film formation at the rate of  $0.0052 \text{ mg/cm}^2/0.25 \text{ hour}$ . This is double the accuracy of the method ( $\pm 0.2 \text{ mg}/77.4 \text{ cm}^2 = \pm 0.0026 \text{ mg/cm}^2$ ). Therefore, the film, detected on the basis of the weight change of the couple, appears to be associated with the stainless steel component. Re-examination of Figure 20, with the realization that the variations in results due to the accuracy of the method tend to cancel out over a series of

TABLE 43. STANDARD HDA PASSIVATION KINETICS <sup>a</sup>

Material	Time Hours	Metal Visual Observations	Acid Analysis-ppm (w/w)				Comments
			Fe	Cr	Ni	Al	
Standard HDA	0	Clear	2	<1	<1	<1	45 wt % $\text{NO}_2$ , 0.3 wt % $\text{H}_2\text{O}$ , 0.7 wt % HF $\text{SV} = 1.1 \text{ in}^{-1}$ (AA), $= 0.3 \text{ in}^{-1}$ (SS)
Std. HDA-AI/SS Cloth	0.25	Acid Clear, Metals Unaffected	2	<1	<1	<1	
	0.5	Acid Clear, Metals Unaffected	2	<1	<1	<1	
	1.0	Acid Clear, Metals Unaffected	2	<1	<1	<1	
	2.0	Acid Clear, Metals Unaffected	2	<1	<1	<1	
	4.0	Acid Clear, Metals Unaffected	3	<1	<1	<1	
	8.0	Acid Clear, Metals Unaffected	3	<1	<1	<1	
	12.0	Acid Clear, Metals Unaffected	4	<1	<1	<1	
	16.0	Acid Clear, Metals Unaffected	4	<1	<1	<1	
	20.0	Acid Clear, Metals Unaffected	4	<1	<1	<1	
	24.0	Acid Clear, Metals Unaffected	4	<1	<1	<1	
	48.0	Acid Clear, Attack on 304 SS remaining wire and underlying AA	5	1	<1	<1	
Aluminum Tubing	48.0	Acid Clear, Metal Unaffected	2	<1	<1	<1	$\text{SV} = 1.1 \text{ in}^{-1}$
304 SS Cloth	48.0	Acid Clear, Metal Unaffected	4	<1	<1	--	$\text{SV} = 0.3 \text{ in}^{-1}$
347 SS Screen	48.0	Acid Clear, Metal Unaffected	5	1	<1	--	$\text{SV} = 0.3 \text{ in}^{-1}$
Std. HDA-AI/SS Screen	48.0	Acid Clear, Red deposit on AA under rusted screen	9	<1	1	<1	$\text{SV} = 1.1 \text{ in}^{-1}$ (AA), $= 0.3 \text{ in}^{-1}$ (SS)

<sup>a</sup>Reference 7.



Reference: Table 24. Passivation Test Data, Test No. 1

**Weight Change**

23.5701 gm - Post Test Weight of Couple, inc. Deposits  
 - 23.5683 gm - Pre Test Weight of Couple  
 -----  
 0.0018 gm - Weight Change, inc. Deposits  
 = 1.8 mg - Weight Change

**Corrosion Rate - Aluminum Alloy**

19.1202 gm - Pre Test Weight of Aluminum Alloy Specimen  
 19.1200 gm - Post Test Weight of Cleaned Specimen  
 -----  
 0.0002 gm - Weight Loss  
 = 0.2 mg - Corrosion

$$\begin{aligned}\text{Corrosion Rate} &= \frac{\text{mg Weight Loss}}{\text{cm}^2 \text{ Test Specimen Area}} \\ &= \frac{0.2 \text{ mg}}{309.6 \text{ cm}^2} \\ &= 0.0006 \text{ mg/cm}^2, \text{ Corrosion}\end{aligned}$$

**Corrosion Rate - Stainless Steel**

4.4491 gm - Pre Test Weight of Stainless Steel Specimen  
 - 4.4495 gm - Post Test Weight of Cleaned Specimen  
 -----  
 0.0004 gm - Weight Gain  
 = 0.4 mg - Film Formation

$$\begin{aligned}\text{Corrosion Rate} &= \frac{0.4 \text{ mg}}{77.4 \text{ cm}^2} \\ &= 0.0052 \text{ mg/cm}^2, \text{ Film Formation}\end{aligned}$$

Figure 34. Passivation Test Calculations

tests suggests that the film formation apparent the first day of exposure of 6061-T4 AA/304 SS couples to Modified HDA, is no longer apparent within a week. Beyond this point, the net effect on the couples is a weight loss due to corrosion. More rapid corrosion was noted at first for the couples exposed to Standard HDA. Beyond seven days, the trend changed, and a rapid buildup of a heavy film ensued. Re-examination of Figure 21, a plot of corrosion rates of aluminum as a function of time, reveals that in Modified HDA, film formation replaced corrosion during the first week. Little change occurred beyond that point. At the end of the test, the change for the aluminum from the couple was equivalent to that of the "blank". Coupling appeared to have no deleterious effect on the aluminum. Corrosion also changed to film formation within a week for aluminum in couples exposed to Standard HDA. The end result was more pronounced than with Modified HDA. Reexamination of Figure 22, a plot of corrosion rates of stainless steel specimens in couples, as a function of time, reveals that, in Modified HDA, film formation gave way to corrosion within one week. Moderate corrosion continued to the end of the test. The final corrosion rate measured for the couple matched that of the "blank". Coupling had no deleterious effect. In Standard HDA, film formation gave way to corrosion within four hours. Beyond that point, corrosion continued at a relatively rapid and constant rate.

The trends and conclusions just described for 6061-T4 AA/304 SS Cloth couples and "blanks" are extended to the entire test matrix in Table 44. Here are contained effects noted from 28 days

of contact between metal/propellant pairs. Film formation was noted for "blanks" of both types of aluminum alloy tested in Modified HDA. A heavier film was noted for 6061-T4 then for 6061-T6. As already noted, coupling 6061-T4 AA to 304 SS Cloth reduced film formation in Modified HDA, but exaggerated it in Standard HDA. Coupling 304 SS Cloth to 6061-T6 led to complete removal of the (lighter) film and resulted in corrosion in Modified HDA. Coupling 347 SS screen to 6061-T4 AA had no effect on the aluminum, when the couple was exposed to Modified HDA. This type of couple was not tested in Standard HDA. The 347 SS Screen "blank" exhibited film formation in Modified HDA, whereas the 304 SS Cloth "blank" was corroded. Coupled with 6061-T4 AA, the 347 SS screen underwent corrosion, but there was no apparent effect on the aluminum. The situation was reversed when 304 SS Cloth was coupled to 6061-T4 AA and exposed to Modified HDA. The corrosion rate of the steel was unchanged, but some of the film on the aluminum was removed. When exposed to Standard HDA, both parts of the 6061-T4 AA/304 SS Cloth couple were adversely effected. Film formation and etching were noted for aluminum; relatively worse corrosion was noted for the stainless steel. Corrosion was also exaggerated in Modified HDA, not only for the aluminum alloy but also for 304 SS Cloth, when 6061-T6 AA was substituted for 6061-T4 AA.

None of the data presented to this point indicate attainment of a passive system during the first 28 days of exposure of metal to acid.

TABLE 44. CORROSION RATES OF COMPONENTS AND COUPLES

Aluminum Alloys					
Test No.	Test Specimen	Type HDA	Exposure Days	CR-AA mg/cm <sup>2</sup>	Comments
24	6061-T4 AA	Modified	28	0.0036	Film.
28	6061-T4 AA/347 SS Screen	Modified	28	0.0036	Film. NE by coupling.
25	6061-T4 AA/304 SS Cloth	Modified	28	0.0016	Film being removed by coupling.
26	6061-T4 AA/304 SS Cloth	Standard	28	0.0607	Heavier Film by coupling. Aluminum etched.
23	6061-T6 AA	Modified	28	0.0016	Film.
27	6061-T6 AA/304 SS Cloth	Modified	28	-0.0023	Film removed by coupling. Aluminum corroded.
Stainless Steels					
Test No.	Test Specimen	Type HDA	Exposure Days	CR-SS mg/cm <sup>2</sup>	Comments
24	347 SS Screen	Modified	28	0.0413	Film.
28	6061-T4 AA/347 SS Screen	Modified	28	-0.0439	Film removed by coupling.
22	304 SS Cloth	Modified	28	-0.0108	Corrosion.
25	6061-T4 AA/304 SS Cloth	Modified	28	-0.0108	Corrosion. NE by coupling.
26	6061-T4 AA/304 SS Cloth	Standard	28	-0.1167	Much more corrosion by coupling.
27	6061-T6 AA/304 SS Cloth	Modified	28	-0.0258	More corrosion by coupling.

Tabulation and graphs of data based on the results of acid analyses performed in support of passivation tests conducted during this program were also presented with some discussion, in Section II. The discussion continues with reference to Figure 35. This figure contains samples of the type of calculation made to test a given acid for saturation with corrosion products of a given metal. For the case chosen, the difference in iron content before and after filtration was found to be 4 ppm. As shown in the same figure, this result lies just beyond the limit of accuracy for the method. It appears, therefore, that the original solution was saturated with an iron species, and that the solubility of iron at the saturation point is in the range of 24 ppm. This value represents the total iron content from all iron species present. As such, the value represents a practical indication of the level of iron content above which particles of corrosion products can be expected to cause filter plugging in propulsion systems. The same type of calculation indicates that the test solution was not saturated with corrosion products of chromium, nickel or aluminum. At levels equal to or below those measured, filter plugging is unlikely.

Reference: Table 26. Passivation Test Results, Test No. 26

Accuracy of Analyses, ppm (w/w)

Fe    - - ± 3  
Cr    - - - ± 2  
Ni    - - ± 2  
Al    - - - ± 7

Test No. 26

28 ppm Fe Before Filtration  
- 24 ppm Fe After Filtration  
-----  
4 ppm Fe . . . . Solution Possibly Saturated with Fe

26 ppm Cr Before Filtration  
- 26 ppm Cr After Filtration  
-----  
0 ppm Cr . . . . Solution Not Saturated with Cr

28 ppm Ni Before Filtration  
- 29 ppm Ni After Filtration  
-----  
- 1 ppm Ni . . . . Solution Not Saturated With Ni

2 ppm Al Before Filtration  
- 2 ppm Al After Filtration  
-----  
0 ppm Al . . . . Solution Not Saturated With Al

Figure 35. Saturation Limit Calculations

Application of the same logic to all of the analyses made in support of passivation tests provided additional data concerning the solubility of corrosion products in Modified HDA and Standard HDA. The results of this exercise are given in Table 45. Herein are contained the concentrations of Fe, Cr, Ni and Al measured after 28 days exposure of the several test specimens to Modified HDA and Standard HDA. The symbol, >, indicates that the solution tested was not saturated with the corrosion products from a given metal. The solubility level lies above the numerical value shown. During Test No. 21, for example, Modified HDA which had been exposed to 6061-T4 AA was not saturated with corrosion products, and the solubility level of aluminum salts lies above 2 ppm Al. The symbol, ~, indicates saturation of an acid with corrosion products of a given metal at a level corresponding to the numerical value shown. During test No. 26 for example, saturation with iron compounds at a level of 24 ppm Fe is indicated, as was discussed with reference

TABLE 45. CORROSION PRODUCT SOLUBILITY DATA FROM PASSIVATION TESTS

Test No.	Test Specimen	Type HDA	Exposure Days	ppm (w/w)					Comments
				Fe	Cr	Ni	Al		
21	6061-T4 AA	Modified	28	.	.	.	> 2		Not saturated with aluminum salts.
24	347 SS Screen	Modified	28	> 9	> 1	> 2	.		Not saturated with stainless steel salts.
28	6061-T4 AA/347 SS Screen	Modified	28	> 13	> 3	> 3	> 2		
22	304 SS Cloth	Modified	28	> 12	> 2	> 2	.		
25	6061-T4 AA/304 SS Cloth	Modified	28	> 11	> 2	> 2	> 2		
26	6061-T4 AA/304 SS Cloth	Standard	28	~ 24	> 26	> 26	> 2		Saturated with Fe in 7 days.
23	6061-T6 AA	Modified	28	..	..	..	> 2		
27	6061-T6 AA/304 SS Cloth	Modified	28	> 10	> 2	> 2	> 2		

to Figure 34. Three additional points, concerning Table 45 deserve mention. First, the data are entirely consistent with the results of corrosion product solubility tests *per se* (Section 2.1). Second, saturation of Standard HDA with stainless steel corrosion products under conditions corresponding to those in the Agena oxidizer tank sump can be expected to occur in approximately one week. Third, no saturation of Modified HDA with corrosion products was noted for any of the tests conducted in this series.

Reference was made in Table 44 to the subject of anodic protection of the components of couples exposed to Standard HDA and Modified HDA during the passivation tests performed as part of this program. Discussion of the subject is continued with reference to Table 46. In this table are summarized conclusions concerning sacrificial anodes drawn by study of data obtained by acid analyses made in support of the passivation tests (Table 26), plots of metal buildup in the acids as a function of time (Figures 23-26), and the corrosion rates of the specimens tested (Table 44). The first entry in Table 46 relates to the 28 day passivation test of a 6061-T4 AA/347 SS Screen couple in Modified HDA. Chemical analyses disclosed a buildup in aluminum content of 2 ppm, and a buildup of 13 ppm Fe, during the test. Corresponding data for "blanks" were 2 ppm Al and 9 ppm Fe. These values agree within the accuracy of the method. If one of the metals were acting as a sacrificial anode, the content of this metal would be much higher for the acid used to test the couple than for the acid used to test the "blank". Conversely, the concentration for the other metal would be higher in the acid used to test the "blank" than in the acid used to test the couple. The measured corrosion rates for the metals likewise fail to disclose the operation of a sacrificial anode. Some of the film on the stainless steel in the couple was removed, as compared with that on the "blank", but there was no measurable effect on the aluminum. Similar reasoning for Test No. 25 ruled out the operation of a sacrificial anode during the 28 day exposure of 6061-T4 AA/304 SS Cloth couples to Modified HDA. The results from analyses used to test the couple were equivalent to the results for the "blanks". Some film was removed from the aluminum in the couple, but there was no difference in the attack on the stainless steel, as compared with the "blanks". No "blanks" were run with Standard HDA, therefore, conclusions concerning Test No. 26, in which a 6061-T4 AA/304 SS Cloth couple was exposed to Standard HDA for 28 days, must be based on the results of the analyses of the acid used to test the couple and the corrosion rates of the components of the couple. These data revealed heavy film formation on the aluminum and severe corrosion of the stainless steel. There was no evidence of a sacrificial anode. Before discussing the final entry in Table 46, further interpretation will be applied to the curves of metal buildup with time in the acids used for 6061-T4 AA and 304 SS Cloth passivation tests. These curves were presented as Figures 23-26 in Section II.

With reference to Figure 23, the buildup of iron in solution, it was noted that Standard HDA was more corrosive than Modified HDA. The course of the corrosion reaction will now be related to the steps involved in these reactions, as represented by the letters A, B and C, placed at appropriate places in the figure. The first reactions may be thought of as a cleaning or pickling process. This process is represented by the letter A. With Modified HDA, the cleaning process took place within the first hour. The next reactions involve surface preparation for corrosion. This process is represented by the letter B. With Modified HDA this process took two days. The combination of processes A and B are the first step in the development of an S-shaped corrosion versus time curve. This step corresponds to an induction period. The next step is steady state corrosion, represented by the letter C. With Modified HDA, this step continued from the second day to the end of the longest test, 28 days. There was no leveling off of this steep part of the S-shaped curve, as would happen once the system became passive. The same steps described for Modified HDA were found for Standard HDA, but the inducted period was shorter, and the corrosion rate was higher. There was some evidence of passivation, but the few samples included for test make this point uncertain. What is clear, however, is the fact that corrosion continued beyond 7 days, where saturation of the acid with iron species was indi-

**TABLE 46. ANODIC PROTECTION DURING PASSIVATION TESTS OF COUPLES**

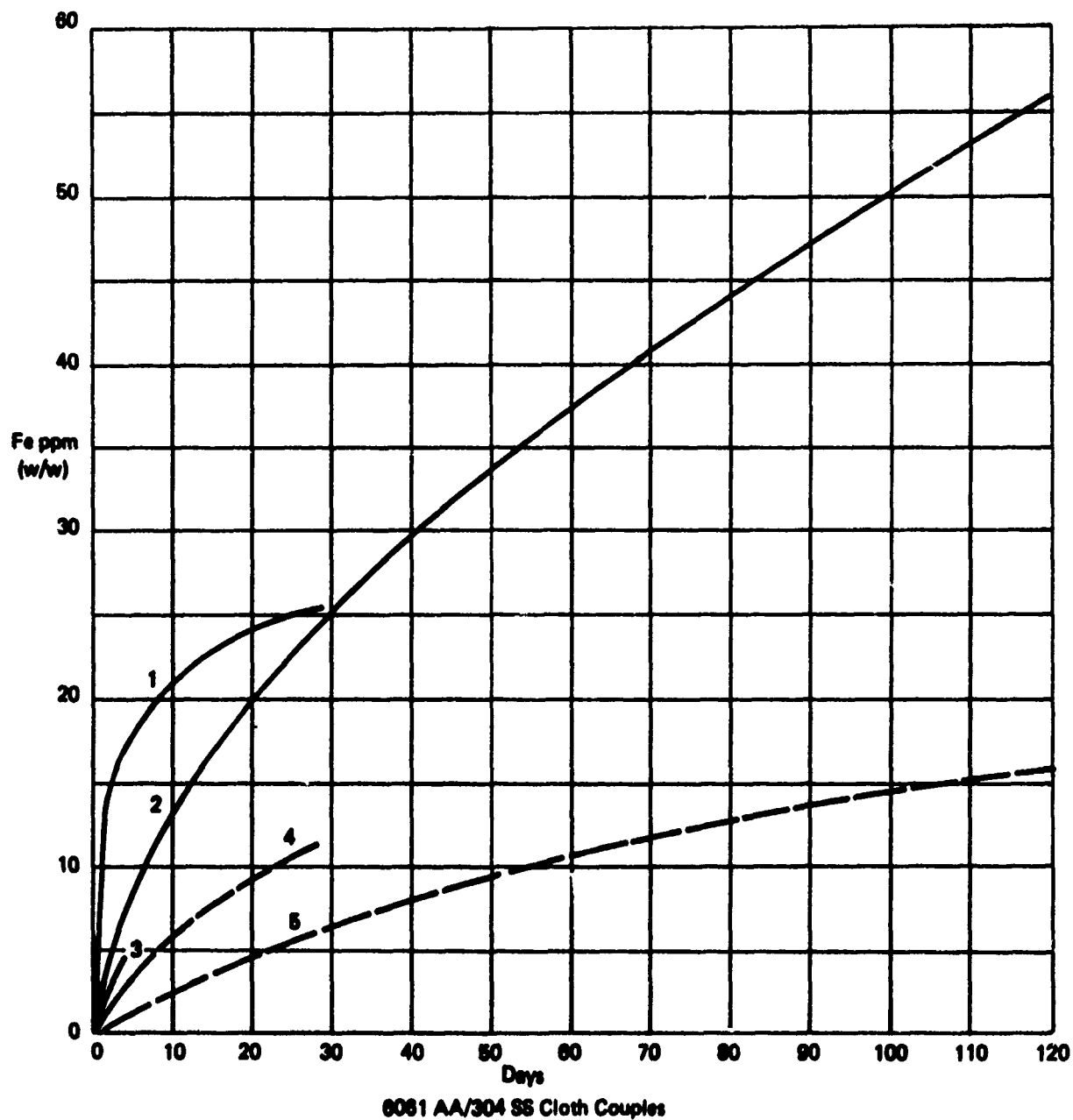
Test No.	Test Specimen	Type HDA	Exposure Days	Sacrificial Anode	Comments
28	0001-T4 AA/307 SS Screen	Modified	28	None	Based on Data in Tables 26 and 44.
25	0001-T4 AA/304 SS Cloth	Modified	28	None	Based on Data in Figures 23-26 and Table 44.
26	0001-T4 AA/304 SS Cloth	Standard	28	None	Based on Data in Table 44.
27	0001-T6 AA/304 SS Cloth	Modified	28	None	Based on Data in Tables 26 and 44.

cated by analyses of filtered samples of acid. This contradicts the theory of corrosion control by saturation of the acid with corrosion products. The fact that no corrosion products were found on the screens post test supports the theory that corrosion is not impeded until a protective film has formed. Figure 24 traces the buildup of chromium in the acids employed for passivation tests. A longer induction period and a relatively small buildup of chromium were noted with Modified HDA. The induction period was shorter and the chromium buildup was much higher in Standard HDA. There was no evidence of stainless steel passivation in either acid. The same trends described for chromium buildup were found for nickel buildup (Figure 25), and the same conclusions follow. Figure 26 traces the buildup of aluminum in the acids employed for passivation tests. No essential difference was found between Modified HDA and Standard HDA. It appears that the induction period was completed within the first day. From this point to the end of the test program, a slow corrosion reaction took place. It might be argued from the shape of the curve(s) on page 2 of Figure 26 that the aluminum had become passive. The weight change data plotted in Figure 20 and the corrosion rate data plotted in Figure 21 negate this interpretation.

Returning to Table 46, the type of reasoning applied previously to discuss other 28 day tests was applied to Test No. 27, involving a couple of 6061-T6 AA/304 SS Cloth exposed to Modified HDA for the same period of time. There was no evidence of an operational, sacrificial anode. Results from analyses of the acids used to test "blanks" matched those for the acid used to test the couple. There was some film removal from the aluminum. There was, however, an accompanying increase in corrosion of the stainless steel.

An overview of all the passivation tests discussed above is presented in Figure 36. This figure contains plots of iron buildup as a function time. The solid curves pertain to tests with Standard HDA. The results from tests with Modified HDA are depicted with broken lines. As can be seen from the accompanying legend, the rate of iron buildup decreased with a decrease in S/V ratio. This was found true for all sets of data with Standard HDA and Modified HDA. This is consistent with the relationship postulated between S/V ratio and corrosion. The higher the ratio, the greater the amount of corrosion in a given time. At a given time, more corrosion is evident for Standard HDA than for Modified HDA. In referring to details about the appearance of the acids samples drawn for analysis, it is found that particles were present in Standard HDA at 30 days for the test represented by Curve 2. Closer definition of their appearance was provided by the data which generated Curve 1. Particles appeared between 7-30 days. These facts have already been used to substantiate the convictions that corrosion rate is not controlled by saturation of the solution with corrosion products. Film formation is advanced as a more likely corrosion control factor. The tendency for the curves to decrease in slope with extension of test time is in keeping with this explanation. It is quite obvious from the curves that effective passivation was never realized in the tests represented, even those of 120 days duration.

Data gathered from other tests of the theory of corrosion control by saturation of the acid being studied with corrosion products are presented in Tables 47 and 48. Table 47 contains the results for analyses of two Standard HDA stock solutions which were similar in composition in all other respects but metals content. One solution was pure. The other solution was contaminated with relatively high concentrations of Fe, Cr, and Ni. Portions of each solution were used for comparative corrosion tests with five different types of stainless steel. Data gathered from these tests are shown in Table 48. The table is arranged in standard corrosion test format, and the explanations given for the tests covered in Tables 43 and 44 apply. The desired comparisons can be made from the "ratings" applied, based on the data currently under consideration. Test No. 404 involved exposure of 17-4 PH H-1025 SS to relatively pure, Standard HDA for 60 days, at 90°F (32°C). The metal/propellant combination earned a very poor rating of 3. The repeat test, 444R, was performed with relatively impure, Standard HDA. According to the solution saturation theory, the rating should have been worse for



Curve	Type HDA	Area AA/SS	SS S/V $\text{in}^{-1}$	Reference
1	Standard	4/1	2.0	This Work
2	Standard	1.4/1	1.0	1
3	Standard	4/1	0.3	3
4	Modified	4/1	2.0	This Work
5	Modified	4/1	1.0	1

Figure 36. Iron Buildup in Solution as a Function of S/V Ratio



TABLE 47. ACIDS FOR TESTS OF CORROSION CONTROL MECHANISMS<sup>a</sup>

Type HDA Used	ppm (w/w)			
	Fe	Cr	Ni	Al
Contaminated, Standard HDA	18	8	6	<1
Pure, Standard HDA	2	<1	<1	<1

<sup>a</sup>Reference 1.

this test than for the original. The rating improved to 2. In the other four comparisons made, the results were equal, not better, when contaminated acid was used rather than pure material. None of these tests supported the solution saturation theory.

Data in support of the theory of film formation for control over corrosion in Modified HDA are provided by further review of results from long term storage tests with this type of acid in small, aluminum and stainless steel tanks, at moderate temperature (Reference 2). These data are summarized in Tables 49 and 50. The first entry in Table 49 corresponds to the results of disassembly and inspection operations after one year of exposure of a 6061 AA tank to Modified HDA, at low ullage (10%). The acid had been removed and was clear in appearance. Chemical analyses revealed an aluminum content of 9 ppm, well below the currently accepted solubility limit. Corrosion rate, calculated from the chemical analysis, was 0.010 mpy (mils per year). No particulate matter was noted inside the empty tank, confirming the conclusion that the acid had not become saturated with corrosion products. The vapor phase area of the tank interior, however, had an iridescent appearance. The liquid phase area was black. Chemical analyses of the interior surfaces of the tank revealed the presence of aluminum fluoride and aluminum phosphate in the discolored areas at the top and bottom of the tank interior. At this point in time, the concentration of the fluoride was higher than the concentration of phosphate. The iridescent areas were attributed to the presence of  $Al_2O_3$  (aluminum oxide). During the second year of test, particles appeared in samples removed from 6061 AA tank S/N-2. This tank was sampled frequently for complete analyses, since it was to be removed from storage at the end of the second year. It therefore had a relatively high ullage. Aluminum content of the acid at the time that saturation with corrosion products appeared was ~ 24 ppm. This value lies within the range of the presently accepted solubility limit. The uncertainty in the measured value derives from the relatively large experimental error for the analysis. Inspection of the tank interior, after the acid had been removed post test, again revealed iridescent areas in the vapor phase, and a black film extending down from the vapor-liquid interface. There was a deposit of white salt near the bottom of the tank. Chemical analyses proved the underlying black film to be predominantly  $AlPO_4$ . This is the salt whose solubility limit appears first to have been exceeded. Subsequent precipitation of the fluoride, oxide and nitrate of aluminum was indicated by the results of analyses of the overlying, white desposit. Analyses of the film on the vapor phase of the tank disclosed traces of the same compounds detected in the deposits. The iridescent areas were proven to be  $Al_2O_3$ . The corrosion rate calculated for 6061 AA, based on the chemical analyses performed at the end of the second year, including allowances for aluminum in the films and deposits, as well as in solution, was found reduced to 0.008 mpy. The processes and results associated with 6061 AA tank S/N-2 were duplicated by S/N-3. The somewhat later attainment of saturation of the acid with corrosion products is attributed to the somewhat lower ullage (and lower S/V ratio) at a given time during the first two years of test. The significant point revealed by post test analyses was the fact that the principal ingredient of the film in the vapor phase was  $Al_2O_3$ . Corrosion rate calculated as before was found to be reduced to 0.006 mpy. These reductions in corrosion reflect film formation, followed by solution saturation with corrosion products. Since total effects

TABLE 48. COMPATIBILITY TEST RESULTS<sup>a</sup>

Test No.	Material (Source)	Cl	Metals										Deposits mg		SNV in. <sup>-1</sup>	Temp. °C		Time Days	Rating <sup>b</sup>	
			Physical Appearance		CR - mpy		CR-mg/cm <sup>2</sup>		Acids Δ wt%		PA									
					Vap.	Liq.	Vap.	Liq.				Vap.	Liq.	M <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>					
					Vap.	Liq.	Vap.	Liq.	Vap.	Liq.	Vap.	Liq.	Vap.	Liq.	Vap.	Liq.	Vap.	Liq.	Vap.	Liq.
					Vap.	Liq.	Vap.	Liq.	Vap.	Liq.	Vap.	Liq.	Vap.	Liq.	Vap.	Liq.	Vap.	Liq.	Vap.	Liq.
404	17-4 PH H-1025 (Shell)	HF	gr-w CPs Etched		0.2	1.8	0.40	5.91	>P	-	0.0126	49	11		1.0	90	32	60	3	
404R	17-4 PH H-1025 (Shell)	HF	w CPs Etched		0.1	0.2	0.43	0.61	>P	-	0.0081	27	11		1.0	90	32	60	2	
405	304 Stainless Steel (Shell)	HF	gr-w CPs Etched		0.1	0.5	0.46	1.04	>P	-	0.0058	35	4		1.0	90	32	60	2	
405R	304 Stainless Steel (Shell)	HF	w CPs Etched		0.1	0.5	0.37	2.04	>P	-	0.0057	11	2		1.0	90	32	60	2	
406	304L Stainless Steel (Shell)	HF	w CPs Etched		0.1	0.3	0.36	1.23	>P	-	0.0061	34	6		1.0	90	32	60	2	
406R	304L Stainless Steel (Shell)	HF	w CPs Etched		0.1	0.2	0.26	0.86	>P	-	0.0045	23	1		1.0	90	32	60	2	
408	301 Ferr Hard SS (Shell)	HF	w CPs Etched		0.1	0.3	0.46	0.94	>P	-	0.0026	15	18		1.0	90	32	60	2	
408R	301 Ferr Hard SS (Shell)	HF	w CPs Etched		0.1	0.4	0.45	1.62	clear	-	0.0047	8	13		1.0	90	32	60	2	
409	302 Cond. B SS (Shell)	HF	>w CPs Etched		0.3	0.9	0.93	2.95	>P	-	0.0374	82	25		1.0	90	32	60	2	
409R	302 Cond. B SS (Shell)	HF	w CPs Etched		0.3	0.5	0.26	2.04	>P	-	0.0045	24	9		1.0	90	32	60	2	

<sup>a</sup>Reference 1.<sup>b</sup>Refer to Table 42 for Rating Scheme.

TABLE 49. COMPOSITION OF FILMS ON TEST TANKS FOR MODIFIED HDA<sup>a</sup>

Tank S/N	Alloy	Exposure Months	Particulate Matter		Films	
			White	Black	Vapor Phase	Liquid Phase
1	8061 Aluminum	12	..	..	AlF <sub>3</sub> , AlPO <sub>4</sub>	AlF <sub>3</sub> , AlPO <sub>4</sub>
2	8061 Aluminum	24	AlF <sub>3</sub> , Al <sub>2</sub> O <sub>3</sub> , Al (NO <sub>3</sub> ) <sub>3</sub>	AlPO <sub>4</sub>	AlF <sub>3</sub> , Al <sub>2</sub> O <sub>3</sub> , Al (NO <sub>3</sub> ) <sub>3</sub> , Al PO <sub>4</sub>	AlF <sub>3</sub> , Al <sub>2</sub> O <sub>3</sub> , Al (NO <sub>3</sub> ) <sub>3</sub> , AlPO <sub>4</sub>
3	8061 Aluminum	36	AlF <sub>3</sub> , Al <sub>2</sub> O <sub>3</sub> , Al (NO <sub>3</sub> ) <sub>3</sub>	AlPO <sub>4</sub>	Al <sub>2</sub> O <sub>3</sub>	AlF <sub>3</sub> , Al <sub>2</sub> O <sub>3</sub> , Al (NO <sub>3</sub> ) <sub>3</sub> , AlPO <sub>4</sub>
1	347 Stainless Steel	12	..	..	F <sub>2</sub> PO <sub>4</sub> ≡	F <sub>2</sub> PO <sub>4</sub> ≡
2	347 Stainless Steel	18	..	..	MF <sub>x</sub> , M(NO <sub>3</sub> ) <sub>x</sub> , M(PO <sub>4</sub> ) <sub>x</sub>	MF <sub>x</sub> , M(NO <sub>3</sub> ) <sub>x</sub> , M(PO <sub>4</sub> ) <sub>x</sub>
3	347 Stainless Steel	36	..	..	MF <sub>x</sub> , M <sub>2</sub> O <sub>x</sub> , M(NO <sub>3</sub> ) <sub>x</sub> , M(PO <sub>4</sub> ) <sub>x</sub>	MF <sub>x</sub> , M <sub>2</sub> O <sub>x</sub> , M(NO <sub>3</sub> ) <sub>x</sub> , M(PO <sub>4</sub> ) <sub>x</sub>

<sup>a</sup>Reference 2.

TABLE 50. THICKNESS OF FILMS ON TEST TANKS FOR MODIFIED HDA

Tank S/N	Alloy	Exposure Months	mils	
			Optical Microscopy	Electron Microscopy
3	6061 Aluminum	36	0.147	0.151
3	347 Stainless Steel	36	0.307	0.393

are averaged by calculations to mils per year corrosion, the reduction in corrosion rate noted is in accord with expectations. The first entry in Table 49 for stainless steel tanks subjected to storage with Modified HDA contains data gathered on disassembly and inspection of a companion tank to 6061 AA tank S/N-1, removed after one year of storage. The acid drained from the tank post test was clear in appearance, and contained 22 ppm Fe. More important, it contained less than 5 ppm Cr. Chromium is the element whose compounds control corrosion according to the solution saturation hypothesis. The value measured falls below the currently expected solubility limit. Inspection of the tank interior, however, revealed the presence of a pale, green film. Positive tests were obtained for metallic fluorides and phosphates in the film: phosphates were more predominant than fluorides. The corrosion rate for 347 SS tank S/N-1 was calculated to be 0.003 mpy. Tank S/N-2 was removed from test prematurely because of leakage, following failure of the temperature control for the environmental chamber used to store the tanks. The failure resulted in overheating ( $\sim 200^{\circ}\text{F}$  ( $93^{\circ}\text{C}$ )) for several hours. The pressure rise in the tanks accompanying the temperature overshoot overtaxed the seal on 347 SS tank S/N-2. Analyses of acid samples taken to that point (19 months) showed values for chromium content below the solubility limit. This corresponded with the fact that no particles of corrosion products were seen in the acid. A film was found in the tank, post test, and chemical analyses were performed to establish its identity. Metal fluorides ( $\text{MF}_x$ ), metal nitrates ( $\text{M}(\text{NO}_3)_x$ ) and metal phosphates ( $\text{M}(\text{PO}_4)_x$ ) were found, where  $\text{M} = \text{Fe}, \text{Cr}, \text{Ni}$ . Conclusions concerning this type of film must be withheld since the film may have been a residue from evaporation of acid left in the tank after the temperature overshoot. The corrosion rate calculated from reliable acid analyses, however, was found to have decreased to 0.002 mpy. The third stainless steel tank completed three years of storage without incident. Chromium content of the acid, post test, was still below the saturation limit, as were the concentrations of iron and nickel. The acid appeared clear. Inspection of the tank interior revealed a definite green film. Chromium fluoride was identified in the vapor phase film. The mixture found in S/N-2 was definitely present in the liquid phase film formed through corrosion of S/N-3. These films are credited with reducing the average corrosion rate for 347 SS tank S/N-3 to 0.001 mpy.

Data concerning the thickness of the films formed in the aluminum and stainless steel tanks exposed to Modified HDA for 3 years are presented in Table 50. Segments cut from the liquid phase of each type of tank were subjected to optical measurements, which disclosed a heavy film (0.147 mil) on the aluminum alloy, and a still heavier film (0.307 mil) on the stainless steel. These measurements were confirmed by emp, to assure that the reported values did not include any of the base metal. The segments have since been sent to the University of Nottingham for independent analyses and evaluation.

No tests of the type performed with Modified HDA were performed with small aluminum and stainless steel tanks filled with Standard HDA. The value of such tests is immediately evident.

## IV. CONCLUSIONS AND RECOMMENDATIONS

### 1.0 CONCLUSIONS

1.1 Pycnometric measurements of the density of Modified HDA confirmed that, at a given temperature, and a given water content, blends containing 42 wt % nitrogen dioxide have the highest density. Density decreases moderately on departure from this nitrogen dioxide level, over the range of 42-46 wt % nitrogen dioxide. Larger changes in density, at a given temperature, and a given nitrogen dioxide content, occur when water content is varied from 0.1-1.0 wt %. The lower the water content of the Modified HDA blend being studied, the higher the density, at constant nitrogen dioxide content and temperature.

1.2 The density of a given blend of Modified HDA increases in a regular manner with a decrease in temperature. Data can, therefore, be extrapolated from one temperature to another over the range studied. Parallel curves are generated when the data for the blends of the type studied are plotted. The slope of the curves is  $-0.0020 \text{ gm/cm}^3/^{\circ}\text{C}$ . This value is in close agreement with reported data for Standard HDA and HDA containing no corrosion inhibitor.

1.3 A higher value was found for density calculated from specific gravity, as determined with a hydrometer, for a given blend of Modified HDA, than was measured pycnometrically. A random pattern was found for the variations for the nine Modified HDA blends studied. These variations are attributed to "buoyancy effects" associated with hydrometers. Errors in density as large as 0.3% were observed for data from hydrometer readings. Variations of this magnitude would bias rocket engine performance calculations involving weight flow as determined from volumetric flowmeters.

1.4 The pressure generated by a given blend of Modified HDA, in a partly filled test vessel, rises in proportion to temperature. Systematic variations in the nitrogen dioxide, water and phosphorous pentafluoride contents of the blends disclosed that the variable which exercises greatest control over the final pressure, at a given temperature, is the nitrogen dioxide content of the acid.

1.5 The pressure developed by a given Modified HDA blend at a given ullage and temperature, the equilibrium pressure, decreases when the ullage space is increased. These decreases are attributed to a decomposition pressure component, as well as a vapor pressure component, of equilibrium pressure. From the magnitude of the pressure changes, it was deduced that nitrogen dioxide is the principal constituent of the vapors above Modified HDA. The decomposition pressure component is due to oxygen. The decomposition component comprises approximately 3% of equilibrium pressures measured.

1.6 Solubility limits for aluminum and stainless steel corrosion products in Modified HDA and Standard HDA were found to depend more on the species of metal compound present than on the temperature, nitrogen dioxide content, or water content of the acids, over the ranges studied. In turn, the metal species present depend on the pretreatment of the metal corroded, the amount of ullage space, and the corrosion inhibitor used. Conditions which promote oxide formation, such as large ullage, lead to corrosion product particles at relatively low metal concentrations. The solubility limit of a given species is reduced by the presence of a common ion of that species, either anion or cation. Solubility limits for the species of a given metal are not appreciably different in Modified HDA or Standard HDA.

1.7 Saturation of Standard HDA with corrosion products occurs more quickly than with Modified HDA, because of the lower corrosion rates associated with Modified HDA. Under conditions such as found in the Agena oxidizer tank sump, Standard HDA generated sufficient stainless steel corrosion products to exceed the solubility of iron species within one week. Corresponding tests with Modified HDA encountered no precipitation within one month, the duration of the test.

1.8 The tests conducted under conditions found in the sump revealed no passivation of the metals tested. After a well marked induction period, corrosion continues at a constant rate for at least one month.

1.9 Data from solubility and passivation tests support a theory that corrosion control in Modified HDA depends on formation of a protective film on the metal exposed to the acid. The process of film formations takes several months.

1.10 Sacrificial anodes were not detected when couples of aluminum alloy and stainless steel were tested in Modified HDA or Standard HDA.

## **2.0 RECOMMENDATIONS**

2.1 Density data required for rocket engine performance calculations should be determined with a pycnometer rather than a hydrometer.

2.2 A pycnometer of practical design, along the lines of the one used for this program, should be developed for routine measurements, at constant temperature.

2.3 The density of Standard HDA should be measured as functions of temperature and acid composition.

2.4 A two cube factorial experiment should be conducted to evaluate the vapor pressure and decomposition pressure of Standard HDA, as functions of temperature, acid composition and ullage. An improved procedure for measuring the exact concentration of nitrogen dioxide for the blends studied should be developed as part of the program.

2.5 The vapor pressure and decomposition pressure components of equilibrium pressure above a given blend of acid should be considered by designers of propellant tanks and turbine pumps.

2.6 Storage tanks should be dedicated to service with a given type of HDA. Ullage space should be kept to a minimum.

2.7 Additional tests with pure fluorophosphates and higher concentrations of corrosion products should be performed to better define solubility limits in Modified HDA. Improvements in the accuracy of analyses for metals should be included as part of the program.

2.8 Additional tests should be performed with Standard HDA to better define the solubility of corrosion products as functions of acid composition and temperature.

2.9 Additional tests should be conducted to determine if the film formation theory of corrosion control for metals exposed to Modified HDA applies to Standard HDA.

2.10 The design of future solubility and passivation test matrices should be developed after review of the data available to date with proponents of a theory of corrosion control, by saturation of a given acid with corrosion products, at the University of Nottingham.

## V. REFERENCES

1. "Agena/ISPS Component Compatibility Study," H. Ph. Heubusch, Bell Aerospace Textron, AFRPL-TR-78-10, March 1978.
2. "Long Term Storage of Modified HDA," H. Ph. Heubusch, Bell Aerospace Textron, AFRPL-TR-76-96, May 1977.
3. "Standard HDA Gel Study," H. Ph. Heubusch, Bell Aerospace Textron, Letter Report No. 6:843, 19 November 1976.
4. "Equilibrium Pressures of Solutions of Nitrogen Dioxide in High Concentrations of Anhydrous Nitric Acid and Corresponding Densities," A. Klemenc and J. Rupp, Journal of Inorganic and Analytical Chemistry, 194, 51 (1930).
5. "Results of Physical Characterization of IMDFNA," E.A. Lawton, Rocketdyne, Letter Report 70RC9682, 2 September 1970.
6. "A Pycnometer Technique for Density Determination of High Density Acid," I.A. Dee, Air Force Rocket Propulsion Laboratory, Technical Memorandum 75-18, September 1975.
7. "Modified HDA Studies," H. Ph. Heubusch, Bell Aerospace Textron, AFRPL-TR-73-77, October 1973.
8. "Military Specification, Propellants, Nitric Acid," MIL-P-7254F, 30 April 1975.
9. "HDA Corrosion Chemistry," C.C. Addison, N. Logan, Nottingham University, AFRPL-TR-77-65, December 1977.
10. "HDA Analyses," J.D. DeBolt, Lockheed Missiles and Space Company, VAFB, Unpublished Notes, November 1976.



## VI. LIST OF ABBREVIATIONS AND SYMBOLS

Abbreviation or Symbol	Description or Meaning and Units
AA	Aluminum Alloy
AA > SS	More Aluminum Alloy than Stainless Steel corrosion products
Al	Aluminum
AlF <sub>3</sub>	Aluminum Fluoride
AlF <sub>3</sub> · 2H <sub>2</sub> O	Aluminum Fluoride, dihydrate
Al(PO <sub>2</sub> F <sub>2</sub> ) <sub>3</sub>	Aluminum Difluorophosphate
Al(PF <sub>6</sub> ) <sub>3</sub>	Aluminum Hexafluorophosphate
Al(NO <sub>3</sub> ) <sub>3</sub>	Aluminum Nitrate
Al(NO <sub>3</sub> ) <sub>3</sub> · 6H <sub>2</sub> O	Aluminum Nitrate, hexahydrate
Al <sub>2</sub> O <sub>3</sub>	Aluminum Oxide
Al PO <sub>4</sub>	Aluminum Phosphate
Al PO <sub>4</sub> · 2H <sub>2</sub> O	Aluminum Phosphate, dihydrate
atm	Atmosphere (pressure)
avg	Average
Bal.	Balance
C	Clear acid, no particles visible
°C	Degrees Celsius
Cap.	Capillary Tube
CH <sub>2</sub> Cl <sub>2</sub>	Methylene Chloride
cm	Centimeter
cm <sup>2</sup>	Square Centimeter
cm <sup>3</sup>	Cubic Centimeter
CPs	Corrosion Products
CR	Corrosion Rate
Cr	Chromium
Cr F <sub>3</sub> · 3H <sub>2</sub> O	Chromium Fluoride, trihydrate
Cr(PF <sub>6</sub> ) <sub>3</sub>	Chromium Hexafluorophosphate
DP	Decomposition Pressure
emp	Electron Microprobe
F	Fluorine atom
°F	Degrees Fahrenheit
F <sup>-</sup>	Fluoride ion
Fe	Iron
FeF <sub>3</sub>	Ferric Fluoride
FeF <sub>3</sub> · 3H <sub>2</sub> O	Ferric Fluoride, trihydrate
Fe(PF <sub>6</sub> ) <sub>3</sub>	Iron Hexafluorophosphate
Fe <sub>2</sub> O <sub>3</sub>	Iron Oxide

## VI. LIST OF ABBREVIATIONS AND SYMBOLS (CONT)

Abbreviation or Symbol	Description or Meaning and Units
g	Green or gaseous
gm	Gram
gm/cm <sup>3</sup>	Grams/cubic centimeter, density
gn-w	Pale green
h	Capillary rise, cm
H <sub>2</sub> O	Water
HDA	High Density Acid, Fuming Nitric Acid, containing 42 ± 2 wt% Nitrogen Dioxide
HF	Hydrofluoric Acid
HNO <sub>3</sub>	Nitric Acid
ibid	Same as above
in <sup>-1</sup>	Reciprocal inch
in <sup>2</sup>	Square inch
ISPS	Integrated Secondary Propulsion System
°K	Degrees Kelvin, absolute temperature
K <sub>sp</sub>	Solubility Product, moles/liter
L	Liter, volume
Liq.	Liquid phase exposure
LMSC	Lockheed Missiles and Space Company
M <sub>2</sub> O <sub>3</sub>	Metal Oxides
memb.	Teflon membrane
mg	Milligram
mg/cm <sup>2</sup>	Milligrams/square centimeter, corrosion rate
mpy	Mils per year, corrosion rate
min.	Minute
Modified HDA or Mod. HDA	High Density Acid, containing 0.5 ± 0.1 wt % Phosphorus Pentafluoride as corrosion inhibitor
n	Mole
N	Nitrogen Atom, or Normality
N <sub>2</sub>	Nitrogen
N/A	Not applicable
NE	No effect
Ni	Nickel
NiF <sub>2</sub>	Nickel Fluoride
Ni(PF <sub>6</sub> ) <sub>2</sub>	Nickel Fluorophosphate
Ni(NO <sub>3</sub> ) <sub>2</sub> · 2H <sub>2</sub> O	Nickel Nitrate, dihydrate
No.	Number
NO <sub>2</sub>	Nitrogen Dioxide

## VI. LIST OF ABBREVIATIONS AND SYMBOLS (CONT)

Abbreviation or Symbol	Description or Meaning and Units
O	Oxygen atom
O <sub>2</sub>	Oxygen
O.K.	Acid with a few, fine particles
p	Partial pressure
P <sub>1</sub>	Pressure in Test Vessel No. 1
P	Pressure, phosphorous atom, or acid with too many particles
>P	Acid with far too many particles
PA or Phys. Appear.	Physical Appearance
PF <sub>5</sub>	Phosphorous Pentafluoride
PO <sub>4</sub> ≡	Phosphate ion
ppm	Parts per million
psia	Pounds/square inch, absolute pressure
PVT	Pressure, Volume, Temperature
Pyc. ID	Pycnometer Identification
S	Solubility, moles/liter
SI	Slight
S/N	Serial Number
SpG 60/60°F	Specific gravity at 60° Fahrenheit
SS	Stainless Steel
SS/Al	Stainless Steel and Aluminum corrosion products
SS > AA	More Stainless Steel than Aluminum Alloy corrosion products
Standard HDA or Std. HDA	Fuming Nitric Acid, Type IV, containing 0.7 ± 0.1 wt % Hydrogen Fluoride as corrosion inhibitor
S/V	Surface-of-metal to Volume-of-acid ratio
t	Time
T	Temperature
T°F	Degrees Fahrenheit, temperature
T <sub>i</sub>	Temperature in Test Vessel No. 1
Temp.	Temperature
V	Volume of capillary to lower index, cm <sup>3</sup>
V <sub>1</sub>	Volume of Test Vessel No. 1, cm <sup>3</sup>
V <sub>k</sub>	Standard Volume, cm <sup>3</sup>
Vap	Vapor phase exposure
Vol	Volume, cm <sup>3</sup>
VP	Vapor Pressure
W	Weld
w	White or weight of gas
w/w	Weight/weight
wt %	Weight percent

## VI. LIST OF ABBREVIATIONS AND SYMBOLS (CONT)

Abbreviation or Symbol	Description or Meaning and Units
~	Approximately or similar to
[ ]	Concentration
°	Degrees, temperature
$\rho$	Density
$\Delta$	Difference
>	Greater than
$\gg$	Much greater than
$\geq$	Equal or greater than
"Hg	Inches of Mercury, pressure
<	Less than
$\mu$	Micron
-	Negative test result
--	No analysis made
+	Positive test result
$\propto$	Proportional to
$\Sigma$	Sum
17-4 PH H-1025	17-4 PH Stainless Steel, H-1025 heat treat conditions
6061-0	6061 Aluminum Alloy, annealed
6061-T4 AA	6061 Aluminum Alloy, T4 heat treat condition
6061-T4 AA/304 SS Cloth	Couple of 6061-T4 Aluminum Alloy and 304 Stainless Steel Cloth
6061-T4 AA/347 SS Screen	Couple of 6061-T4 Aluminum Alloy and 347 Stainless Steel Screen
6061-T6 AA	6061-T6 Aluminum Alloy, T6 heat treat condition
6061-T6 AA/304 SS Cloth	Couple of 6061-T6 Aluminum Alloy and 304 Stainless Steel Cloth